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Nuclear magnetic resonance and knight shift of cadmium in dilute alloys

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NUCLEAR MAGNETIC RESONANCE AND KNIGHT SHIFT OF CADMIUM IN DILUTE ALLOYS

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APPROVAL SHEET

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ABSTRACT

The nuclear magnetic resonance of ^{113}Cd has been investigated in dilute binary alloys with indium, silver, and magnesium solutes in an effort to isolate the parameters controlling the anomalous temperature dependence of the cadmium Knight shift. Changes in the Knight shift produced by alloying have been measured at 4.2°K, 78°K, 300°K, and 423°K, employing a static magnetic field of 12 kilogauss.

All observed changes in the isotropic Knight shift are small, and may be accounted for in terms of Friedel oscillations or the rigid band model. From changes in line shapes it is concluded that alloying magnesium decreases the anisotropic Knight shift of cadmium. It is concluded that changes in the c/a ratio, changes in the energy gap at points K in the Brillouin zone, and changes in the diamagnetic susceptibility may be ruled out as major sources of the thermal behavior of the isotropic Knight shift in pure cadmium. The data appear to be in agreement with a recent pseudopotential calculation which attributes the temperature dependence of the isotropic shift in cadmium primarily to the pronounced d-character in the pseudopotential and the effects of lattice vibrations.

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INTRODUCTION

Cadmium is a divalent metal, crystallizing in a hexagonal close-packed structure. It has a c/a ratio of 1.886 at room temperature, which deviates from the ideal value of 1.633 by more than any other hexagonal metal. Consequently cadmium exhibits marked anisotropies in its electronic properties, such as magnetic susceptibility[1] and electrical resistivity.[2]

Nuclear magnetic resonance (NMR) can provide information about the electronic structure of solids as a result of the effect on the nuclei of various interactions with the electrons. In metals the most important of such interactions are the hyperfine interaction between the conduction electrons and the nuclei, and the nuclear quadrupole interaction between nuclei which possess intrinsic electric quadrupole moments and electric field gradients generated by anisotropic electronic charge distributions. Since the cadmium nuclei involved in the NMR studies reported here have spin ½ they possess no quadrupole moments. Therefore the basic interaction involved in this research is the hyperfine interaction, which in metals gives rise to an effect known as the Knight shift.

The isotropic Knight shift (K_{iso}), attributable to the Fermi contact term in the hyperfine Hamiltonian, is in most metals only weakly dependent on temperature. In cadmium K_{iso} is markedly temperature dependent,[3,4,5] increasing by about 70% in the range from 1 to 594°K, at which

temperature the solid melts, and undergoing an additional 33% increase in this phase transition.

Because of the anisotropic crystal structure of cadmium, it also may, and does, possess an anisotropic Knight shift (K_{an}), resulting from that term in the hyperfine Hamiltonian coupling the nuclear magnetic dipole moments with the electronic magnetic dipole moments. K_{an} in cadmium also shows an increase with temperature, having a small negative value of -0.01% at 1°K and a rather large value of +0.05% at the melting point.[3,4,5,6]

At the beginning of this investigation the strong temperature dependence of K_{iso} and K_{an} in cadmium was not yet adequately explained; the motivation for this work was a desire to obtain experimental data which isolate the parameters controlling the thermal variation of the Knight shift in cadmium. Recently, however, Kasowski and Falicov[7] have published a theory which accounts for this behavior. The data obtained in this investigation appear to be in agreement with the theory of Kasowski and Falicov.

By adding small amounts of other metals to cadmium, one can modify the electron concentration and charge distribution and thus change the Knight shift. This modification of the Knight shift in dilute alloys is interpretable in terms of the alloy theory of Friedel oscillations[8] of the electronic charge density in the vicinity of the impurity atoms. Verkin[9] has studied the influence of alloying magnesium into cadmium through its effects on the magnetic susceptibility of these dilute alloys. The addition of magnesium, which is homovalent to cadmium, produces quite large changes in the temperature variation of the magnetic susceptibility.

The Fermi surface of cadmium has many features in common with zinc, which is also a divalent hexagonal close-packed metal. Zinc, however, has small pockets of electrons, called needles, at points K on the vertical edges of the hexagonal Brillouin zone. (Please refer to Figure 5 for the designation of major symmetry points in the Brillouin zone.) These needles are absent in cadmium. Adding magnesium to cadmium decreases the c/a ratio, as does lowering the temperature. Since varying the c/a ratio changes the dimensions of the Brillouin zone, alloying permits one to alter the relation between energy surfaces and zone edges. It is actually possible to cause the appearance of the needles at points K at a particular temperature and magnesium concentration, which manifest themselves by a pronounced peak in the diamagnetic susceptibility. Since small pockets of electrons, in conjunction with small energy gaps and small effective masses are known to have marked influence on the diamagnetic susceptibility, Verkin maintains that the susceptibility variations he observes are attributable to changes in the portion of the Fermi surface at points K in the Brillouin zone, changes in the width of the gap associated with this surface at the Brillouin zone boundary, and modifications of the c/a ratio.

The measurements of the Knight shift and its variation with temperature in these alloys should therefore provide information for a decision as to whether the temperature dependence of the Knight shift in cadmium can be attributed to any of the following phenomena: (1) changes in the c/a ratio; (2) variations in the electron concentration; (3) changes in the Fermi surface about points K; (4) alteration of the small gap at the zone edge; (5) variations in the magnetic susceptibility.

In the following sections of this paper the theory and background of this problem will be considered, the experimental techniques will be outlined, and the experimental results will be presented and interpreted in the light of the theory of Kasowski and Falicov.

THEORY AND BACKGROUND

ISOTROPIC KNIGHT SHIFT

When the NMR frequency in a metallic sample is observed, it is found that this frequency differs from that detected for the same nuclear species in a diamagnetic compound, both measurements having been performed in the same static magnetic field. This displacement of the NMR frequency in metals is called the Knight shift, after its discoverer, W. D. Knight.[10] Since this shift is generally an order of magnitude or more greater than chemical shifts, it was realized that such a shift is associated with the conduction electrons of the metal.

The Knight shift has been successfully explained in terms of the hyperfine interaction between the nucleus and the non-localized conduction electrons. Starting from the Fermi contact term in the hyperfine Hamiltonian,

$$H_{en} = \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \sum_{j,1} \vec{I}_j \cdot \vec{S}_1 \, \delta(\vec{r}_1 - \vec{R}_j)$$

where $\vec{r}_1$ is the position vector of the 1^{th} electron, $\vec{R}_j$ the position vector of the j^{th} nucleus, γ_e is the gyromagnetic ratio of the electron, γ_n is the gyromagnetic ratio of the nucleus, $\vec{I}$ is the nuclear spin angular momentum, and $\vec{S}$ is the electron spin angular momentum, one obtains the following expression for the Knight shift, K:

$$K \equiv \frac{\Delta H}{H_0} = \frac{\Delta \nu}{\Delta_0} = \frac{8\pi}{3} \left\langle |u_k(0)|^2 \right\rangle_{E_F} \chi_p \ .$$

In this expression u_k (0) is the conduction electron wave function at the nucleus, $\langle\ \rangle_{E_F}$ denotes an average taken over the Fermi surface, and χ_p is the Pauli electronic susceptibility, given by the relation

$$\chi_p = \mu^2\ N(E_F),$$

where μ is the Bohr magneton and $N(E_F)$ is the density of states at the Fermi surface. The temperature dependence of χ_p is very slight for normal metals, being proportional to T/T_F, where the Fermi temperature T_F is given by the expression $E_F = k_B T_F$. k_B is the Boltzmann constant.

This relation for what is now termed the isotropic Knight shift, K_{iso}, has been satisfactorily confirmed for the alkali metals, and appears to be valid for many other metals. K_{iso} was found to be independent of frequency or field, to be usually positive, to increase with increasing atomic number, and to display little or no dependence on temperature.[11]

From measurements on cadmium by Seymour and Styles,[3] Schone,[6] and Borsa and Barnes,[4] it became apparent that K_{iso} in cadmium exhibited a large and anomalous dependence on temperature, shown in Figure 1. It was also observed, by Seymour and Styles,[3] that K_{iso} in cadmium underwent a large positive jump on passing through the melting point, amounting to about 33% of its value just below the melting point. Most metals show only a small increase in K_{iso} through the melting transition.

Various mechanisms were suggested to account for the unusual behavior of K_{iso} with temperature, but none of these arguments was carried through in sufficient detail to be able to claim that a theory for the temperature dependence of the Knight shift existed prior to the work of Kasowski and Falicov.[7]

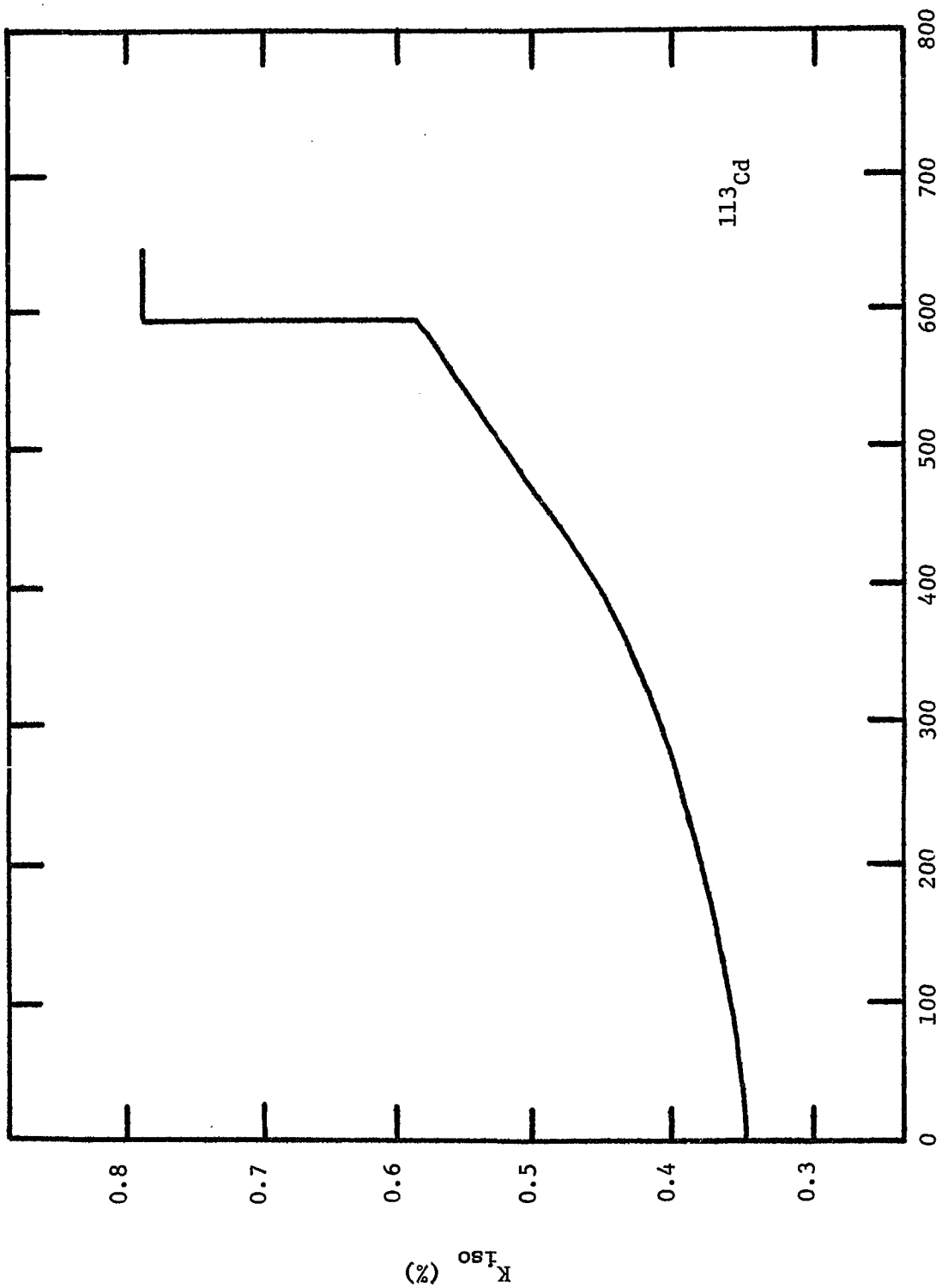

Figure 1. The isotropic Knight shift of pure cadmium versus temperature.

An obvious candidate for investigation is the correlation between the temperature dependence of K_{iso} and the magnetic susceptibility, whose temperature dependence in cadmium is shown in Figure 2. A major experimental difficulty occurs immediately. Theory predicts that K_{iso} depends on the electronic part of the magnetic susceptibility, not on the bulk susceptibility which is generally measured. Only in lithium and sodium has the electronic susceptibility been measured separately. Not only is the bulk susceptibility due to the sum of a term for the ion-core susceptibility and the electronic susceptibility, the latter term depends in a complicated way on many factors -- small details of the Fermi surface, the existence of small energy gaps at Brillouin zone boundaries, the effect of small pockets of electrons or holes, and the possibility of interband transitions. Thus the connection will, of necessity, be rather indirect.

Another possible cause of the anomalous temperature behavior of K_{iso} was the variation of the c/a ratio with temperature resulting from the anisotropic elastic properties of cadmium.[12,13] However from isothermal measurements of changes in the Knight shift induced by hydrostatic pressures as high as 8000 kgm/cm^2, Kushida and Rimai[14] concluded that c/a ratio changes contribute only a small fraction of the temperature dependence of the Knight shift in cadmium. Because of the pronounced anisotropy in the elastic constants of cadmium, their measurements were very nearly a determination of the response of K_{iso} to uniaxial pressure.

Since K_{iso} depends on the s-character of the conduction electron wave function it is possible that a variation of the percentage of s-character and p-character with temperature could lead to the observed behavior of K_{iso}. Such a change in character of the electronic wavefunctions would be expected from motion of a portion of the Fermi surface

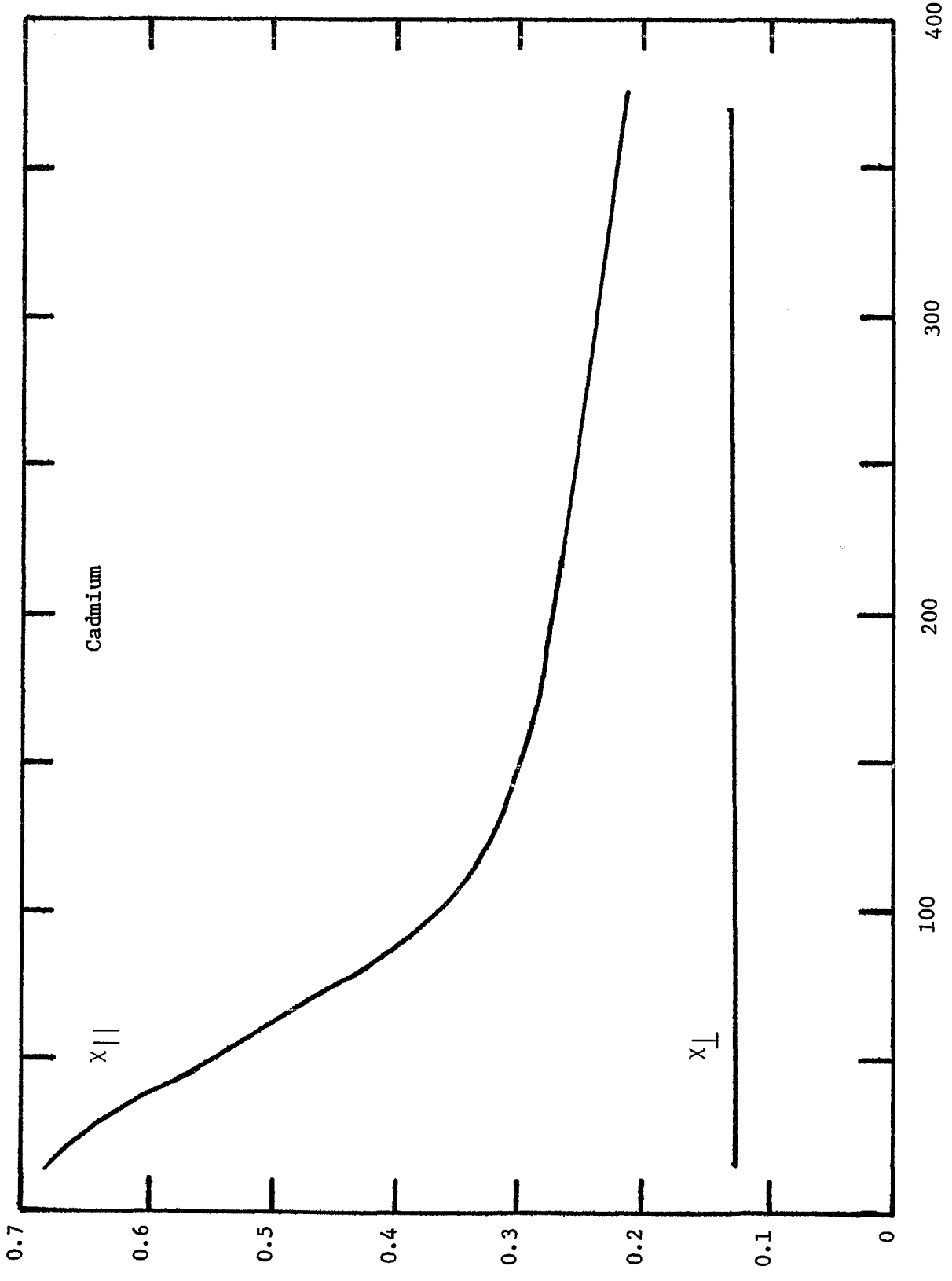

Figure 2. Temperature dependence of the [illegible]

toward or away from a zone boundary, as suggested by Cohen and Heine.[15] Further, since what enters into the theory for K_{iso} is an average over the Fermi surface of the s-type wave functions, changes in the Fermi surface will, in general, influence the average. Kasowski and Falicov have found that the Fermi surface in cadmium does vary more significantly with temperature than is usually observed in metals.[7]

Finally, it was also suggested that magnetic breakdown might be involved,[4] but no details were presented. Magnetic breakdown refers to a phenomenon in which electrons become able to cross forbidden energy gaps and thus travel in different orbits than were possible before the breakdown occurred. Tsui and Stark[16] have observed significant magnetic breakdown effects on their de Haas - van Alphen data at a field of 25 kilogauss and temperatures below 4.2°K. Recently Ruvalds[17] has obtained an expression for the electronic susceptibility which includes magnetic breakdown contributions. Since all data in this research were obtained at 12 kilogauss no magnetic breakdown effects were observed.

ANISOTROPIC KNIGHT SHIFT

For a metal with symmetry lower than cubic, the spin dipolar term in the hyperfine Hamiltonian,

$$H_2 = -\gamma_e \gamma_n \hbar \vec{I} \cdot \left(\frac{\vec{S}}{r^3} - \frac{3\vec{r}(\vec{S}\cdot\vec{r})}{r^5} \right)$$

leads to an additional contribution to the Knight shift. This contribution may be conveniently written in terms of a shift parallel to the crystal axis and one perpendicular to that axis in the form

$$K_{||} = K_{iso} + 2\chi_p q$$

$$K_{\perp} = K_{iso} - \chi_p q ,$$

where

$$q = \left\langle \int \psi^{*}_{\vec{K}} \frac{(3z^2 - r^2)}{r^5} \psi_{\vec{K}} \, d^3 \vec{r} \right\rangle_F$$

Here $\langle \rangle_F$ denotes an average over the Fermi surface. The quantity q is essentially the degree of anisotropy of the electronic charge of the states at the Fermi energy. The difference between $K_{||}$ and $K_{\perp}$ is generally called the anisotropic Knight shift, K_{an}. That is,

$$K_{an} = K_{||} - K_{\perp} .$$

In a polycrystalline sample the anisotropic contribution to the position of the NMR line averages to zero. Consequently there is no net shift in the line position resulting from this anisotropic interaction, but there is a field dependent broadening of the line and an asymmetry provided by K_{an}. Figure 3, adapted from a paper by Masuda,[48] illustrates the effects of K_{an} on the NMR line shape.

Cadmium, being hexagonal, also shows an anisotropic Knight shift.[4,5,6] As is the case with K_{iso}, K_{an} also possesses a pronounced temperature dependence. Figure 4 shows K_{an} as a function of temperature.

From the expression for K_{an} and the definition of the quantity q it is seen that only p- or higher character in the electronic wave functions can contribute to K_{an}, since component wave functions of s-character give q a value of zero.

Just as a variation in the percentage of s- and p-character of the electronic wave functions might lead to the temperature dependence of K_{iso}, it is clear that such an effect would also influence the temperature dependence of K_{an}. Further, any or all of those factors

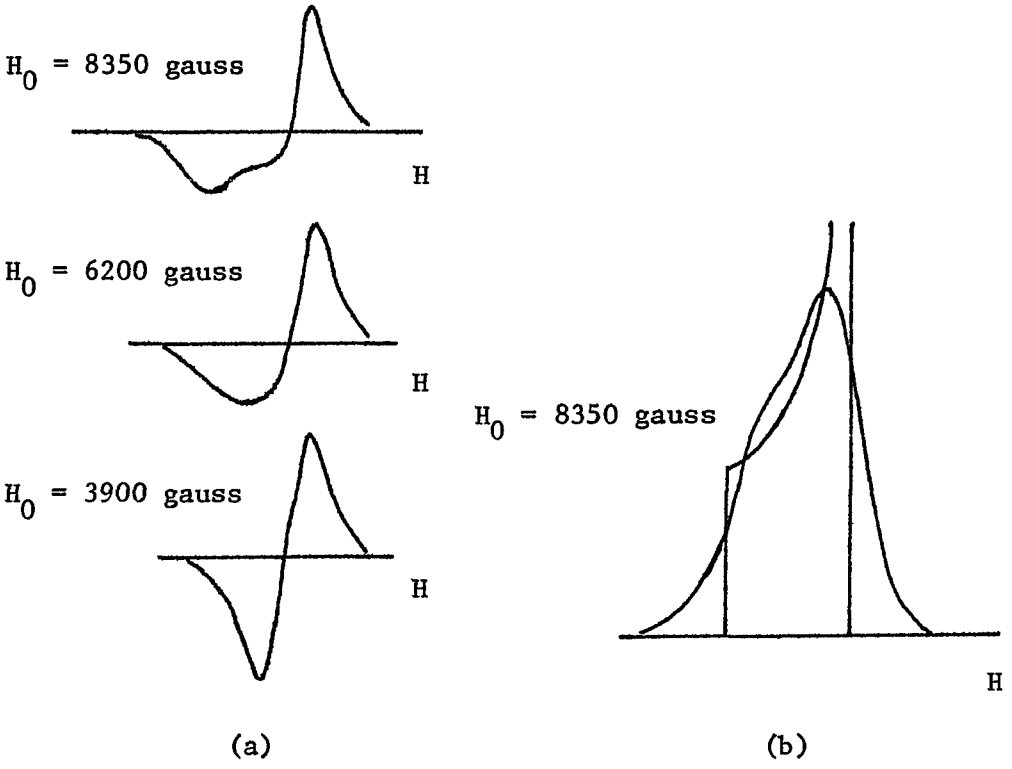

Figure 3. The Influence of K_{an} on NMR Line Shape.

(a) Illustration of the effect of the anisotropic Knight shift on the NMR derivative line for pure cadmium powder samples.

(b) The NMR absorption line shape at a field of 8350 gauss, shown dressed onto the anisotropic broadening function.

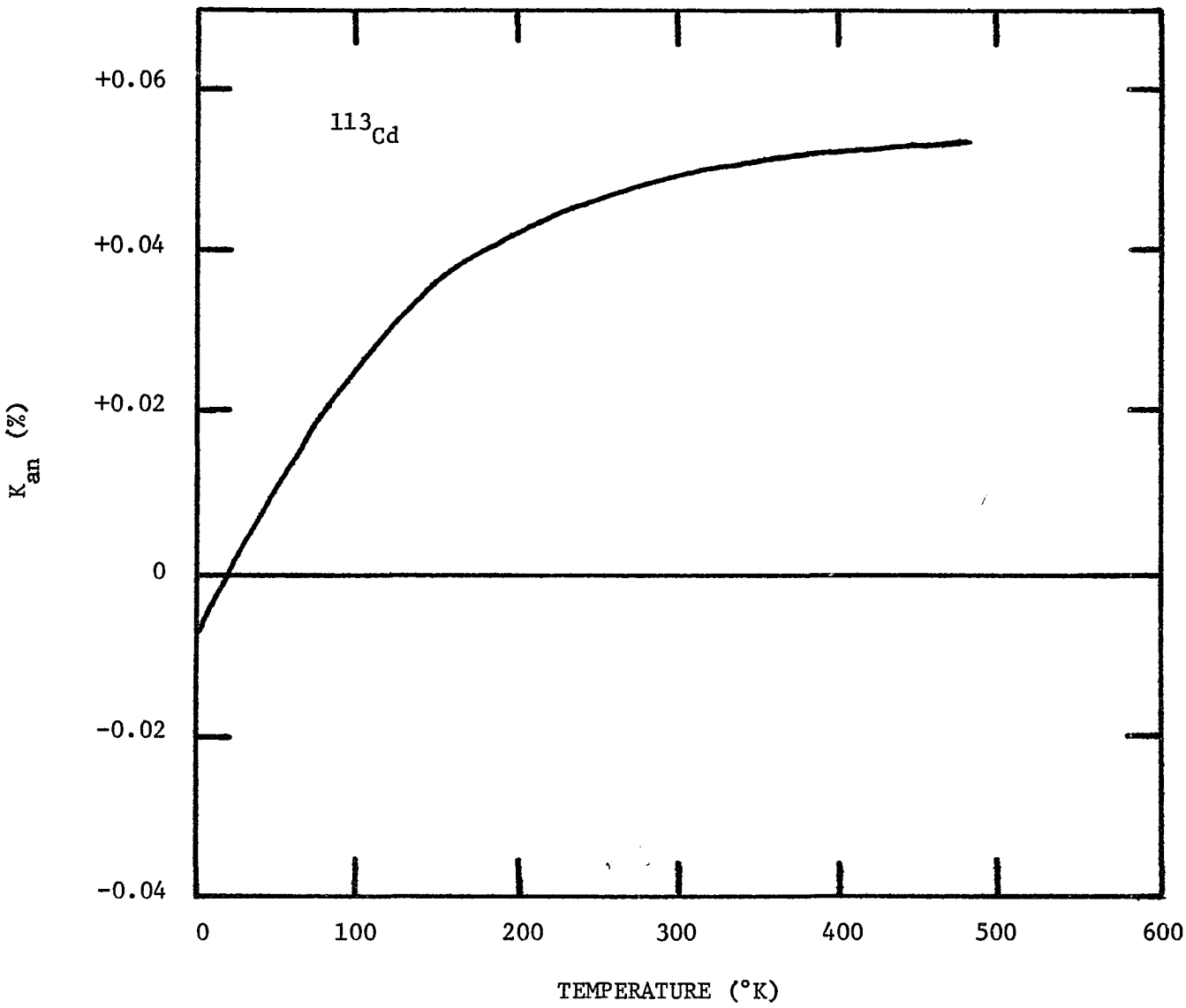

Figure 4. The anisotropic Knight shift of pure cadmium versus temperature.

connected with a temperature variation of the electronic susceptibility might contribute to the thermal behavior of K_{an}.

If one uses an oriented single crystal, the experimental determination of K_{an} is quite direct. One merely needs to measure $K_{\perp}$ and $K_{\parallel}$. Schone[6] used this technique with cadmium. However, since it becomes increasingly difficult to observe the NMR in a single crystal as the temperature is increased, powder samples are usually employed. An indirect procedure for determining K_{an} from data on powder samples is discussed in detail by Borsa and Barnes,[18] involving a study of the field-dependent line width. Essentially, they showed that the peak-to-peak line width at high magnetic field is a valid measure of K_{an}.

ALLOYS

The introduction of impurities into a metal has two effects on the NMR observed in that metal: (1) the NMR line broadens; (2) there is usually a shift in the resonant frequency for a given field. The change in the position of the solvent NMR line can be attributed to a change in the Knight shift, ΔK, resulting from oscillatory variations in the conduction electron charge density about the solute ions. The line broadening is a consequence of the same charge redistribution phenomenon; since the solute ions are randomly distributed, solvent nuclei at different distances from an impurity will suffer different shifts in their resonance frequencies. This spread in resonance frequencies, when summed over all the solvent nuclei, produces line broadening. This phenomenon is similar in some respects to the broadening caused by the anisotropic Knight shift in a powder sample of pure cadmium. It should be noted that the line

broadening due to alloying will be field dependent. The broadening of the line in the powder samples due to K_{an} will likewise be field dependent. Since the two sources of line broadening will be competitive in the samples investigated in this research, it should be expected that the two effects will be difficult to separate out experimentally. At 78°K and 4.2°K, however, where K_{an} is quite small, it should be possible to observe the alloy broadening effects, since then the effects of the anisotropic Knight shift on the NMR line shape and width are small; this was found to be the case for the cadmium-silver alloys. Because the rule devised by Blandin and Daniel[19] that line width should increase proportionally to the square root of the concentration was obtained on the explicit assumption of the absence of other major sources of line broadening, it is to be expected that such a concentration dependence will not be observed in the alloys of cadmium studied here. Indeed, the data on the alloys of silver and copper analyzed by Blandin and Daniel[19] show only a feeble agreement with the square root rule.

In order to assess the adequacy of the Blandin-Daniel theory[19] for the alloys of cadmium investigated here it will be useful to discuss their theory and the assumptions entering into it. They consider only the case of heterovalent alloys. Electrical neutrality requires a redistribution of the conduction electrons so as to produce a screening of the perturbing potential presented by the impurity ion. It is assumed that this screened perturbing potential is spherically symmetric and limited in range to the atomic sphere of the impurity ion. Explicitly assuming a free-electron model and Bloch functions they use standard scattering theory in order to calculate an expression for $\Delta\rho(\vec{r})$, the

change in the electronic charge density introduced by the shielded impurity potential, in terms of phase shifts in the free-electron wave functions. Invoking the proportionality of the Knight shift to the electronic charge density at the nucleus they obtain the simple expression

$$\frac{\Delta K_j}{K} = \frac{\Delta\rho(\vec{R}_j)}{\rho}$$

where ΔK is the change in Knight shift experienced by the nucleus at $\vec{R}_j$. To represent the impurity potential they choose a spherical well with the same radius as the solute ion and a depth sufficient to attract the electronic charge required for the screening. They invoke the Friedel sum rule connecting the phase shifts with the impurity charge and use Blatt's phase shifts,[20] which accommodate any size effects by means of an effective charge, to calculate a spectrum of Knight shifts for silver in the alloys Ag Cd, Ag In, and Ag Sn. Finally to obtain an expression for the average Knight shift of the solvent nuclei in low concentration heterovalent alloys they further assume a random substitutional alloy, that electrons on the Fermi surface undergo no multiple scattering from the dissolved impurities, and that the net excess electron density at a nucleus is a simple sum of excess densities due to each isolated impurity, whence

$$\frac{\overline{\Delta K}}{K} = c \sum_1 (\alpha_1 \sin^2\eta_1 + \beta_1 \sin 2\eta_1),$$

where c is the concentration, η_1 are the phase shifts, and α_1 and β_1 are combinations of spherical Bessel and Neumann functions of argument kR.

The only other assumption entering into their prediction for line broadening, mentioned earlier in this section, is that the broadening due to impurities is much greater than the line width characteristic of the pure solvent.

The following observations are offered concerning the applicability of the theory of Blandin and Daniel,[19] outlined above, to the data obtained in this study.

The large change in K_{iso} when cadmium melts would seem to imply that cadmium is less free-electron like than most metals. Ziman[21] has argued that the small change observed in the Knight shift for most metals indicates that a free-electron picture of metals is more nearly correct than was previously recognized. The band structure calculations for cadmium by Stark and Falicov,[22] using the pseudopotential formalism and a semi-empirical pseudopotential obtained from de Haas-van Alphen data[23,16] also support the conclusion that cadmium is less free-electron like than most metals. Thus it might be expected that the Blandin-Daniel theory[19] will have less pertinence for cadmium alloys than the silver or copper alloys to which it was originally applied.

The assumptions in their theory of a spherical Fermi surface, purely s-character for the electronic wave functions, and an effective mass identical to the normal electron mass, would also appear to be suspect in view of the band structure calculations and Fermi surface data referred to above.

The Blandin-Daniel theory[19] includes only changes in the electron density. No consideration is given to possible changes in the

magnetic susceptibility produced by alloying. This is certainly questionable, since the Knight shift is known to depend on the electronic susceptibility. Although changes in susceptibility could be incorporated into a refined version of the scattering theory through changes induced in the density of states at the Fermi surface by phase shifts, such a refinement has not yet been attempted, probably because comparisons between theory and experiment have so far been only semiquantitative at best.

Finally, the Blandin-Daniel theory[19] is only appropriate when the solvent and solute have different valences. Since cadmium and magnesium are homovalent, their theory can not be applied to any of the data on cadmium-magnesium alloys obtained in this research, even though scattering and phase shifts still occur. More will be said concerning the last two points in the section on magnetic susceptibility.

A conceptual scheme which is frequently employed in considering the properties of alloys is the so-called rigid band model.[24] For a pure metal the electronic structure may be fairly well accounted for on the basis of present theory. Employing single-particle Bloch functions, the energy structure of the pure metal is adequately described in terms of Brillouin zones, energy gaps, energy bands, a Fermi surface, density of states, etc.[25] The simplest form of the rigid band model of alloys assumes that the constant energy surfaces and density of states characteristic of the solvent are not modified by alloying. The consequences of adding the solute are adding or subtracting electrons from the band, depending on the relative valence of the solute, and either dilating or contracting the Fermi surface, thereby filling or depleting the density-of-states curve. Aside from the simplicity of this model, it has had some

success in explaining certain properties of alloys, such as the Hume-Rothery rules[24] and the c/a ratio changes in hexagonal systems.[26] On the other hand it has failed to explain the electronic specific heat and electronic susceptibility of alloys, both of which depend on the density of states.

Stern[25] has attempted to improve the rigid band model by permitting the density of states in the alloy to be different, but retaining the other assumptions. Arguing under the assumptions of the rigid band model, he points out that the single-electron eigenstates of the pure solvent, ε_k, become modified as a result of adding impurities so that a particular Bloch state whose energy in the pure solvent was ε_k will change in the alloy to a state having an energy of the form $E_k + i\Gamma_k$, and consequently will no longer be an eigenstate. For small impurity concentrations, however, he assumes that Γ_k will be small compared to the bandwidth, Δ, and may be neglected for calculating the properties of dilute alloys. Then the change in energy of a Bloch state upon alloying may be written as $\Delta E_k = E_k - \varepsilon_k$. He further assumes that this change in energy depends only on ε_k, and not on k, claiming that this assumption appears to be valid when the perturbation due to the impurity is fairly localized about the solute site. Stern next shows that if ΔE_k is a constant the density of states curve for the alloy would have the same shape as that of the pure solvent, but would be displaced in energy by an amount ΔE_k. However ΔE_k is not in general a constant, and an attempt is made to derive an expression for the variation in the density of states upon alloying. Enroute to his final result, he unfortunately purports to have proved that ΔE_k does not depend on either

the impurity potential or the impurity mass. In a footnote he points out that is has been brought to his attention that this proof was fallacious; consequently it is far from clear that his attempt to improve the rigid band model has succeeded.

It is probably worthwhile here to mention a recent exchange of opinions between Watson, Bennett, and Freeman[27,28] and Van Ostenburg and Alfred[29] concerning the validity of both the rigid band model and the Friedel oscillations picture in treating the change in Knight shift upon alloying. Watson, et. al., argue that it is incorrect to use only Friedel oscillations in predicting the effects of alloying on K, and present an expression for the electron concentration at the nucleus obtained from the rigid band model alone which includes valence effects and yields ΔK behavior of the magnitude and sign observed experimentally.

Van Ostenburg and Alfred criticize this argument on the ground that an error was made by Watson, et. al., in analyzing the experimental data, and they argue that therefore the conclusion of Watson, et. al., is erroneous. In the later paper[28] Watson, et. al., consider the alleged error in some detail, denying that an error has been committed and reinforcing, and clarifying, their original argument. They observe that the previously mentioned linear dependence of ΔK on concentration predicted by Blandin and Daniel[19] is still moot, that the scattering theory should not assume plane waves, and that one ought not to try to infer susceptibility behavior from specific heat data (the point attacked by Van Ostenburg and Alfred). They conclude by observing that a good theory has not yet been realized.

The cadmium-indium data obtained in this investigation tend to support Watson, et. al.,[28] particularly on the point of linearity of the ΔK versus concentration dependence.

ELECTRONIC MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility of "ordinary" metals, specifically excluding those which are ferromagnetic or strongly paramagnetic, is quite small, being on the order of 10^{-6} cgs units. This susceptibility may be attributed to two different sources, the ion cores and the conduction electrons. The contribution due to the magnetic moments of the electrons bound to the ions of the lattice is diamagnetic and is reasonably well understood. No more will be said about this contribution. The electronic susceptibility contains a paramagnetic term, χ_p, the Pauli susceptibility, which depends only on the density of states, and a diamagnetic term, χ_L, the Landau-Peierls susceptibility, which also depends on the density of states, but whose magnitude relative to χ_p varies as m/m^*[30], where m^* here refers to the entire band and is given by the relation

$$m^* = \left[\frac{1}{h^2}\frac{\partial^2 E}{\partial k^2}\right]^{-1}.$$

The electronic susceptibility of many polyvalent metals exhibits some unusual properties, including temperature dependence. In particular, Zn, Cd, and In have strongly temperature dependent susceptibilities.

Verkin[9] argues that in many cases, including the divalent metals, the temperature dependence of the susceptibility can best be

explained by invoking χ_A, an interband term discussed by Adams.[31] Adams shows that a degenerate electron gas (ignoring any electron-electron interactions) can be diamagnetic only if the average effective mass of the electrons at the Fermi surface is considerably smaller than the free electron mass. For a free electron gas the Landau diamagnetic susceptibility is only one third that of the paramagnetic Pauli term. Adams invokes the idea of small energy gaps leading to small effective masses as a consequence of the large curvature of the energy surface. Thus the large contributions to the Landau-Peierls susceptibility come from regions on the Fermi surface where the electron states in two or more bands are almost degenerate. Two states which are nearly degenerate can be appreciably admixed by what would otherwise be a very weak perturbation, and the second order energy resulting from this admixing will have a magnitude proportional to the reciprocal energy gap. The magnetic field is just such a weak perturbation which can cause such an admixture of states in different bands, and the second-order energy associated with this admixing makes a contribution to the susceptibility. The electronic structures of cadmium and zinc are very similar, except that zinc has electronic needles resulting from a slight overlap of the Fermi surface across a zone edge. Cadmium does not have these needles. At 4.2°K, zinc has a c/a ratio of 1.830 compared to value of 1.863 for cadmium. Verkin[9] reduced the c/a ratio for cadmium by introducing a Mg impurity and found that the appearance of the electronic needles is clearly evidenced by a prominent peak in the diamagnetic susceptibility. He also observed that the susceptibility varies markedly with concentration of Mg, suggesting that the interband term may be quite important for cadmium and its alloys.

These results of Verkin[9] suggested that it might be useful to investigate the Knight shift in Cd-Mg alloys to determine whether the effects of these concentration and temperature dependent susceptibilities were reflected in the shifts themselves. This would permit, perhaps, an explicit correlation of the temperature dependence of the Knight shift in cadmium with the behavior of the magnetic susceptibility, or a denial of such a correlation.

KASOWSKI AND FALICOV'S THEORY

Kasowski and Falicov[7] have recently calculated both the isotropic and anisotropic Knight shifts for cadmium with the pseudopotential formalism. They utilize the pseudopotential devised by Stark and Falicov[20] and incorporate the effects of lattice vibrations directly into their calculations.

The pseudopotential formalism is essentially an extension of the orthogonalized-place-wave technique of Herring.[32] Electronic wave functions are chosen to be combinations of plane wave states and core states in such a fashion that the resulting wave functions are orthogonal to the core states. This choice permits a formal rewriting of the Schroedinger equation in a normal form, with the potential term appearing as a combination of the crystal potential and an effective potential term arising from the orthogonalization process. This pseudopotential is much weaker than the crystal potential. The wave functions entering into the rewritten Schroedinger equation are linear combinations of the orthogonalized plane waves and are called pseudowave-functions. The effect of the orthogonalization enters into the pseudopotential as an

operator. Phillips and Kleinman[33] approximated the operator term in the pseudopotential by a simple repulsive potential. Although the general form of the pseudopotential formalism retains the full operator form of the pseudopotential, it is sometimes possible to achieve good results with a local pseudopotential, which depends on position only. The general form of pseudopotential, depending on more than one variable, is called a non-local pseudopotential.

In order to fit the de Haas-van Alphen data on cadmium Stark and Falicov[22] found that it was necessary to employ a non-local pseudopotential, and that the Fermi surface obtained with their choice of pseudopotential was quite different from what is expected for a hexagonal close-packed nearly free electron metal. It is significant that the Stark-Falicov pseudopotential obtained by empirically fitting the de Haas-van Alphen data yields a Fermi surface which agrees very well with the radio frequency size effect measurements[34] and also with superconductivity data[35] from which the density of states at the Fermi surface may be inferred.

Kasowski and Falicov proceed to calculate K_{iso}, K_{an}, and the Pauli susceptibility at four different temperatures: T = 0°K, 298°K, 462°K, and for the liquid. Qualitatively they describe the temperature dependence of K_{iso} and K_{an} in the following manner:

At T = 0°K the pseudopotential is quite large and mostly d-like, giving rise to a significant decrease in the density of states at the Fermi energy compared to the free-electron density of states. At higher temperatures the lattice vibrations serve to decrease the effective

pseudopotential, causing the density of states to approach a more nearly free-electron value and a consequent increase in the electron spin susceptibility.

The third zone lens is generated by states of mostly s-like and p_z-like character, this character being essentially independent of temperature. (Please see Figure 5 for a sketch of the Fermi surface of Cd).

The first and second-zone monster is formed principally of states which in the vicinity of the ions have mainly s-like and p_x-p_y-like character. The size and shape of the monster is strongly dependent on both the strength and symmetry of the pseudopotential. With increasing temperature the two separate sheets of this hole surface rejoin, yielding a multiply-connected surface similar to the ones found in zinc and magnesium. Additional pieces of electron surface also appear in the third and fourth zones about the points L.

As temperature increases and the pseudopotential becomes both weaker and more isotropic the electronic states on the monster become more s-like and less p_x-p_y-like around the ions. Consequently the s contribution to the average over the Fermi surface increases with the temperature, thus causing K_{iso} to increase with temperature.

Since the p_x-p_y contribution to the wave function average decreases with an increase in temperature, but the p_z part remains essentially unchanged, the p_x-p_y dominance present at low temperatures changes to a large p_z dominance at higher temperatures, causing K_{an} to go from a small negative value at low T to a large positive value at higher T.

Finally, on melting, cadmium becomes a free-electron-like metal and K_{iso} increases by an additional 32% over its value in the solid just before melting.

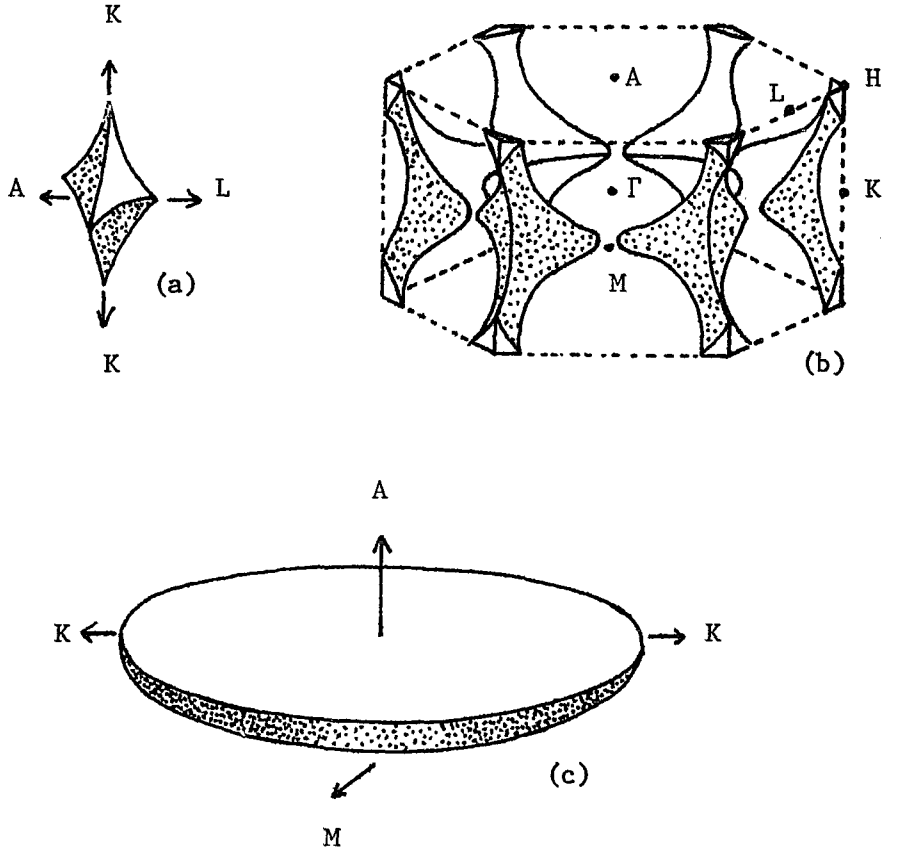

Figure 5. Sketch of free-electron Fermi surface of cadmium at 0°K.

(a) First zone hole pocket centered on H;

(b) Second zone hole monster. The arms of the monster, shown unconnected here at 0°K, join together as the temperature increases to form a multiply connected surface;

(c) Third zone lens centered on Γ.

The designation of major symmetry points in the Brillouin zone is shown in (b).

Their calculated values for K_{iso} and K_{an} agree quite well with experimental data, although the agreement is better for K_{iso} than for K_{an}.

They include exchange and correlation effects through the use of a temperature independent enhancement factor in the spin susceptibility, choosing the factor so as to make their calculated value of K_{iso} agree with the experimental value at low temperature.

Kasowski and Falicov ignore core polarization effects, contending that they are negligibly small.

EXPERIMENTAL CONSIDERATIONS

In this section details of the preparation of the alloy samples will be discussed. A brief discussion of the experimental apparatus used in the detection of the NMR signals will also be presented.

PREPARATION OF SAMPLES

Most of the alloys were made by heating the constituents together in an oven. After carefully weighing the ingredients, in the form of shot or pellets, on a balance to establish the proper concentration for the alloys, the mixture was placed in a glass tube. The tube containing the sample was then evacuated for one to two days with a pumping system capable of providing a pressure less than 10^{-5} mm. of mercury. The sample tube was then sealed off, under vacuum, and suspended in the oven. The sample was then melted by heating to at least 50°C above the melting point of the component with the higher melting temperature. Manual shaking was used to provide adequate mixing of the ingredients. The sample was then quenched and removed from the tube. The melting points of the elements involved are: cadmium, 320.9°C; indium, 156.2°C; silver, 960.8°C and magnesium, 650°C.

The melting points of silver and magnesium are above the softening point of pyrex. Therefore it was necessary to employ Vycor tubes for making the magnesium alloys. Since silver melts at a temperature

even higher than the softening point of Vycor, it was deemed expedient to purchase the cadmium - silver samples, in the form of slugs, from commercial suppliers.

It is worthwhile to mention here that the cadmium - 1/2% silver and the cadmium - 2% silver alloys were ordered from Alfa Crystals and Materials Research Crystals, respectively, as single crystals, the purity of the components being given as 99.999%, on a "best effort" basis, and that in neither instance was a single crystal achieved. Single crystals would have been preferable for this investigation because of the ease and lack of ambiguity in interpreting and analyzing the NMR data. Considerable effort was expended in this laboratory in an attempt to grow single crystals of the cadmium - indium series of alloys. Both the Bridgman method and the zone-melting technique were utilized in this unsuccessful attempt, primarily by Mr. W. G. Rich. Because of the inability to obtain single crystal specimens of the alloys, it was necessary to settle for powder samples. However, single crystals of pure cadmium were grown in this laboratory and employed for reference measurements.

After the alloys were quenched, they were next examined for homogeneity by chemical etchant techniques. First the samples were immersed in a standard cadmium etchant, which is known to act selectively along the few crystal directions, and subsequently in an etchant specific to a solute material. This technique provides a relatively simple and direct determination of both grain size and solute distribution.

When homogeneity of the sample had been ascertained, it was then triturated with silicon-carbide paper. No. 220 grade Wet-or-Dry

paper, glued onto a backing plate which could be mounted in a lathe, was used for this purpose. The resulting powder was caught on a sheet of clean aluminum foil and then sifted through a 200 mesh standard sieve. After obtaining one or two cubic centimeters of the sifted powder, it was poured into a 12 by 75 millimeter test tube and sealed off with a torch.

A radio frequency coil, consisting of 9 turns of #24 enameled wire, was wound directly around the lower portion of the tube containing the sample. When connected into the tank circuit of the marginal oscillator these coils provided an oscillation frequency in the range from 9 to 12 MHz; since the gyromagnetic ratio of cadmium nuclei is 5.93×10^3 $(\text{gauss}\cdot\text{sec})^{-1}$, this frequency was appropriate for obtaining NMR in a static magnetic field on the order of 12 kilogauss. For data taken with the crossed-coil system, the sample tubes were mounted directly inside of a one-turn pick-up coil which is an integral part of the crossed-coil probe.

Since sample preparation was an important part of this study, much care was taken to achieve good quality samples. Many samples were discarded as unsatisfactory after careful examination subsequent to employing the standard metallographic chemical etchant techniques recommended by G. L. Kehl in his book The Principles of Metallographic Laboratory Practice.[36] It is of course true that such techniques afford only a macroscopic test for sample homogeneity, and are not capable of ascertaining sample concentration. Something like electron beam microprobe analysis and mass spectrometer analysis techniques would be required to guarantee concentration accuracies to a high degree.

In two cases, cadmium - 1/2% silver and cadmium - 1/2% indium, two samples were prepared independently and NMR data obtained - in both cases the NMR data agreed to within the experimental error. For cadmium - 1/2% silver one of the samples was purchased from a commercial supplier, the other prepared in this laboratory. It is admitted that the agreement of such data does not prove that sample preparation has been flawless, but such agreement does offer some feeling of confidence.

Solubility data for the alloys employed in this investigation are as follows:

Cd - Ag -- up to 5 atomic % of Ag in cadmium;[37]

Cd - In -- up to 1.4 atomic % In in cadmium in the range 126 - 196°C;[38]

Cd - Mg -- up to 15% Mg in cadmium.[39]

NMR EQUIPMENT

Two separate NMR detection systems, the marginal oscillator and the crossed-coil systems, were used for obtaining the data. Both are standard NMR detection systems of the C-W variety,[40,41] and will be discussed separately below.

Marginal Oscillator System (see Figure 6 for a block diagram of this system.)

The marginal oscillator consists essentially of a variable frequency radio frequency oscillator operated under such conditions that a decrease in Q, occurring as the frequency is swept through the nuclear magnetic resonance, causes a decrease of the level of oscillation. The sample whose NMR is to be observed is placed directly inside of a rf

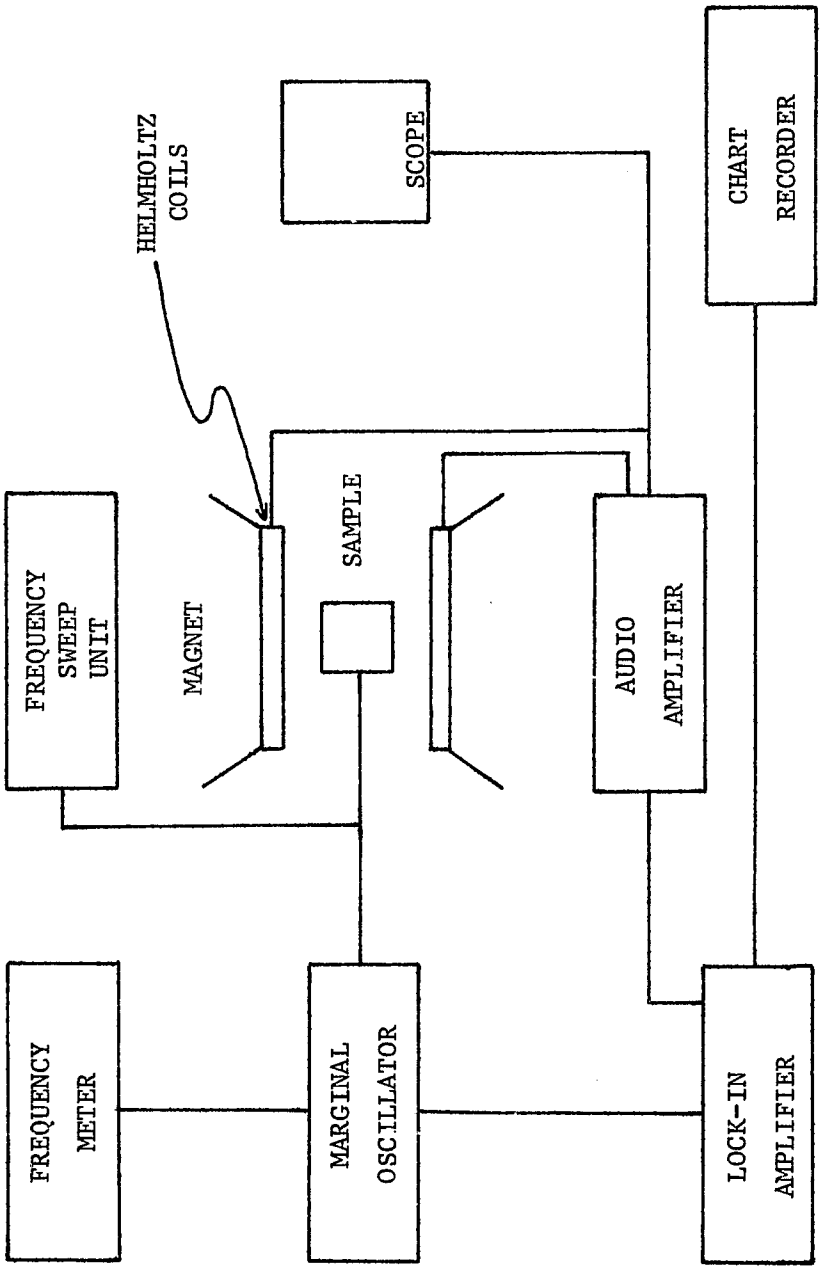

Figure 6. Block Diagram of Marginal Oscillator System

coil which is a part of the tank circuit of the oscillator -- when the sample absorbs rf energy at resonance this represents a decreased Q in the tank circuit, and the change in the level of oscillation may be observed by measuring the rf voltage across this sample-bearing coil. This behavior is apparent in Figure 7 and Figure 8.

In practice several stages of rf amplification and feedback control of the oscillator are employed. The advantages of the marginal oscillator are the following: (1) it permits sweeping frequency, rather than magnetic field; (2) since it responds to changes in resistance only, the resonance line is due entirely to χ'', the absorptive part of the effective susceptibility (except with single crystals or large sample grains, where eddy current mixing of χ' and χ'' can occur, producing a real component of χ_{eff} which is a mixture of χ' and χ''); (3) it is readily adaptable to placing the sample directly into a variable temperature dewar vessel for low temperature measurements -- the sample coil is merely soldered to a coaxial cable by which it is suspended inside the dewar vessel.

The major disadvantage of the marginal oscillator is its low level of oscillation as a result of which the signal to noise ratio may be quite low.

Crossed-Coil System (see Figure 9 for a block diagram of this system.)

In the crossed-coil or nuclear induction scheme, the sample is placed inside separate transmitter and detector coils. These coils are carefully mounted to be orthogonal to each other, so that no transmitter signal can leak into the detector circuit, and mutually orthogonal to the

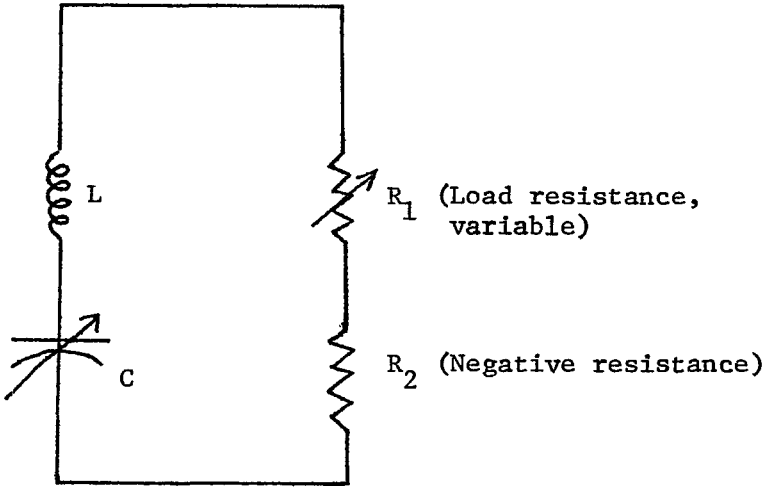

Figure 7. Idealized diagram of marginal oscillator.

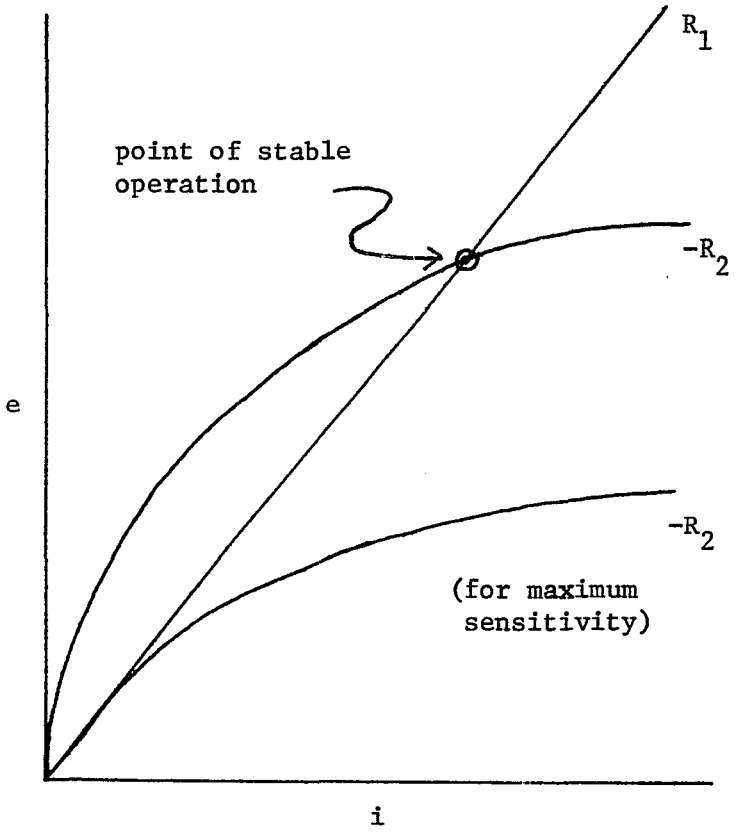

Figure 8. Idealized e vs. i characteristics illustrating marginal oscillator.

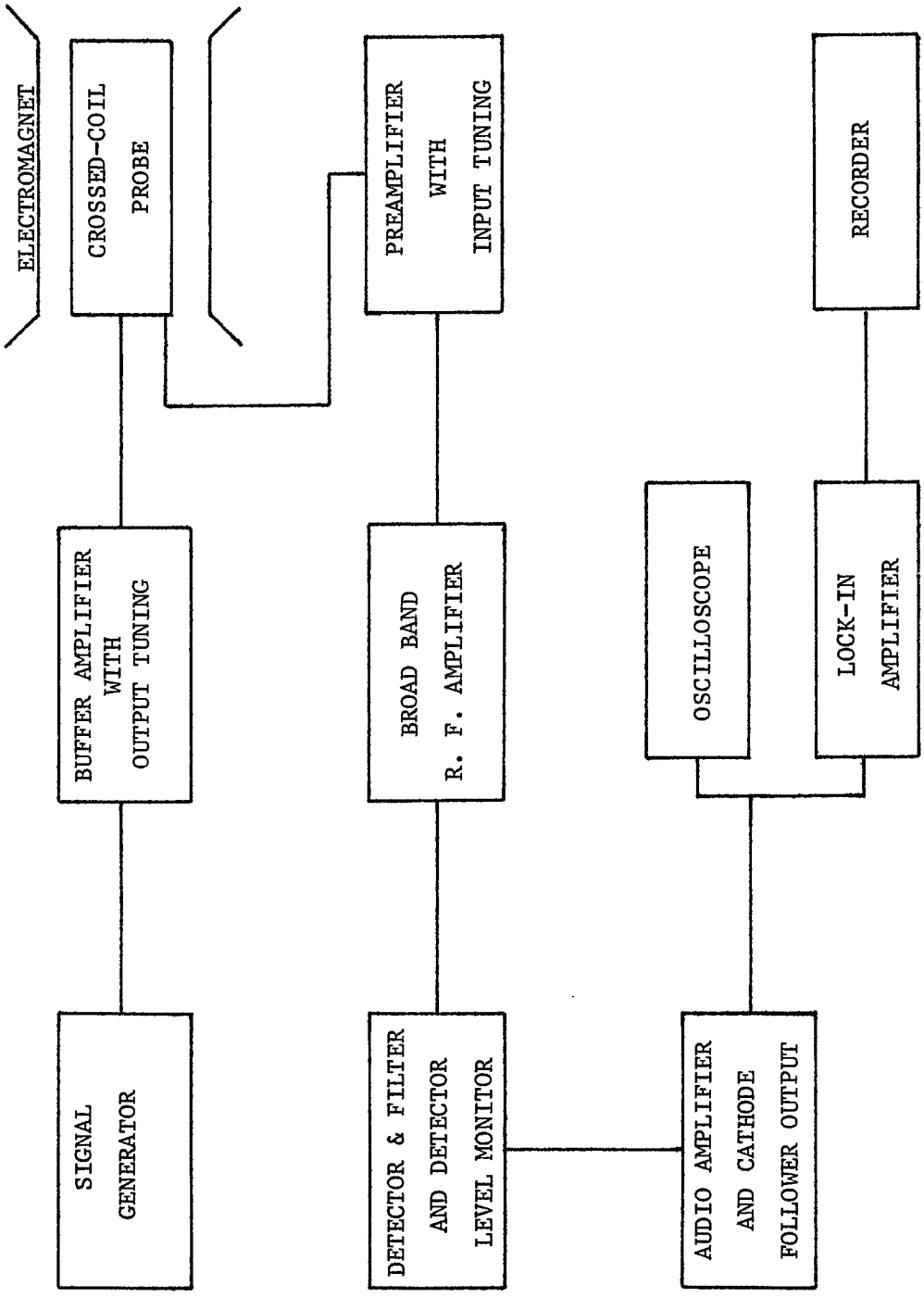

Figure 9. Block Diagram of Crossed Coil System.

static magnetic field. The transmitter, which in this system may be operated at power levels limited only by the onset of saturation, drives the absorptive transitions between adjacent nuclear Zeeman levels. Saturation here refers to a phenomenon whereby, as the amplitude of the applied rf signal, (H_1), is increased, the signal-to-noise ratio of the observed absorption stops improving and begins to decrease again. The observed absorption signal frequently obeys the relation[42]

$$\chi''(\nu_0, H_1) = \chi''(\nu_0, 0) \; [1 + 1/2\gamma^2 \; H_1^{\,2} \; T_1 \; g(\nu_0)]^{-1},$$

where $\chi''(\nu_0, H_1)$ is the imaginary part of the nuclear magnetic susceptibility, γ is the gyromagnetic ratio of the nuclear species whose NMR is being observed, T_1 is the spin-lattice relaxation time, $g(\nu)$ is the shape function of the unsaturated resonance, ν_0 is the resonance frequency, and H_1 is the magnitude of the rotating rf field. Saturation is generally specified by the equality

$$1/2 \; \gamma^2 \; H_1^{\,2} \; T_1 \; g(\nu_0) = 1.$$

A small component of the transmitter signal is permitted to leak into the detector. As the magnetic field is swept slowly through the resonance, the modulation of the small component of the transmitter signal is picked up by the detector coil and then subjected to rf amplification. The crossed-coil detection scheme has the following advantages: (1) the transmitter power can be quite large, provided that T_1, the spin-lattice relaxation time is sufficiently short, thus providing good signal to noise ratios; (2) either the absorption or the dispersion lines may be obtained separately - this may be useful in some circumstances.[42]

The disadvantages of the crossed-coil system are the following: (1) since the transmitter, detector, and flux linkage are all tuned for a particular frequency it is necessary to operate the system in a field-sweep mode, and accurate field measurements are less convenient than accurate frequency measurements; (2) the rigorous geometrical requirements for the crossed-coil probe render it difficult to place the sample in a dewar vessel, making low temperature measurements rather expensive.

GENERAL

Common to both the crossed-coil and the marginal oscillator systems is the use of standard narrow-band detection techniques employing the lock-in amplifier. The use of such a phase sensitive detection scheme is dictated primarily by the low signal to noise ratios of the NMR signals. This requires the use of magnetic field modulation. The reference signal from the lock-in, after amplification by an audio frequency amplifier, is fed to a pair of Helmholtz coils attached directly to the pole pieces of the magnet. A frequency on the order of 100 Hz is typical. If this modulation amplitude is small compared to the NMR absorption line width, one obtains at the output of the lock-in a signal proportional to the derivative of the absorption line. This is seen in Figure 10.

With the marginal oscillator it is both possible and convenient to sweep frequency. This is done by employing a commercially available voltage-variable capacitor in the tank circuit of the marginal oscillator. Its operation depends on the fact that the depletion layer thickness in a reverse-biased p-n junction diode varies with the

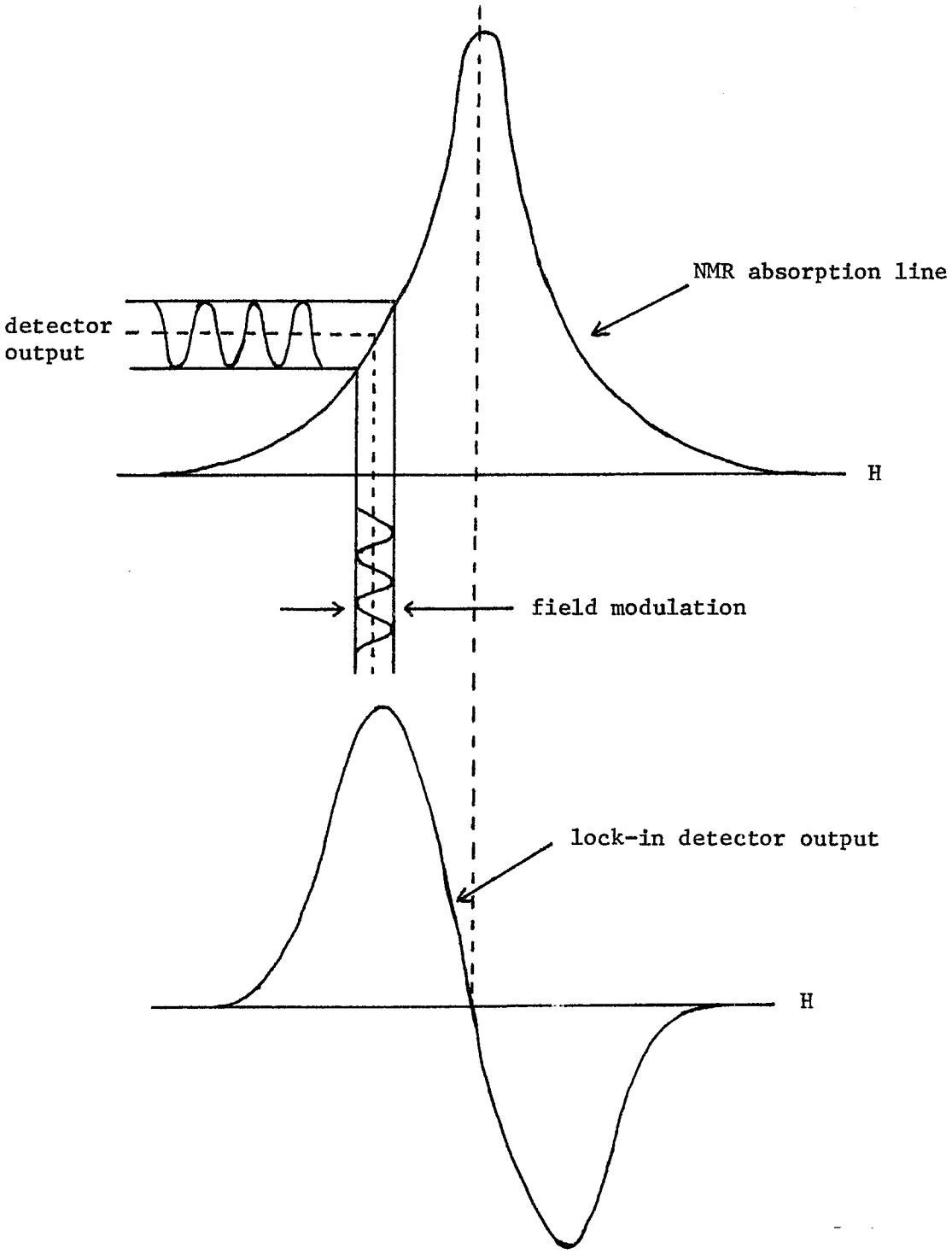

Figure 10. Illustration of the manner in which the derivative of the NMR absorption line is obtained by the use of field modulation small compared to line width.

bias voltage across it. A motor driven potentiometer provides the bias sweep.

As previously mentioned, it is necessary to operate the crossed-coil system in a magnetic field sweep mode. This is done by applying a saw-tooth voltage output from an operational amplifier directly to the current control of the electromagnet.

Two different electromagnets were employed. The one used with the marginal oscillator system was a Magnion electromagnet, capable of providing fields from 0 to 30 kilogauss. It has 15" pole pieces tapered to 6", with a 1 3/4" gap, just large enough to permit the Helmholtz coils to be placed directly on the pole faces and still allow room for the tail section of the low temperature dewar vessel. The sample-bearing coil was placed directly in the cryogenic fluid -- either liquid helium or liquid nitrogen -- inside the inner dewar. By waiting until thermal equilibrium had been obtained, as could be determined by the rf frequency stability, it was possible to be certain that the sample was at the same temperature as the coolant. Typically two or three hours were required to achieve thermal stability at liquid nitrogen temperature; equilibrium at liquid helium temperature was attained in only two or three minutes as a consequence of the large value of thermal diffusivity at that temperature.

Field homogeneity was determined to be better than 0.1 gauss over the sample volume of approximately 1 cubic centimeter.

The magnet used with the crossed-coil system was a Magnion electro-magnet, with field variable from 0 to 12 kilogauss. This magnet has 12" pole pieces and a 2" gap, providing ample space for the Varian probe. Field variation over the sample volume was less than 0.1 gauss.

In order to detect any field variation during the scan of an NMR line, a metallic sodium reference, suspended just outside the dewar, was utilized. Sodium NMR lines were run prior to recording the alloy NMR lines, and again immediately afterwards.

To eliminate time constant effects (tending to displace the line from its true position) all alloy lines were swept through by both lowering and raising the frequency, the average value being taken as the correct position. Since care was taken to employ sufficiently low sweep rates, well within the requirements of the 10 second output time constant of the lock-in amplifier, the averaging procedure produces reliable results. Modulation effects on linewidth and shape were minimized by using as low a value of field modulation as signal to noise ratio would permit, typically about 1/4 of the line width. It is estimated that the error in the NMR line widths is less than 10% for data obtained at 4.2°K and 78°K, and considerably less than 10% for the wider NMR lines obtained at 300°K.

Since most of the measured shift values were quite small, the pure cadmium powder NMR line was recorded so that differences could be determined directly from the recorded data.

The high-temperature data was obtained with the crossed-coil system. Heating of the sample was accomplished by mounting the sample tube inside a small glass dewar vessel, located inside the sample cavity of the Varian probe, and blowing hot air over the sample tube. Temperature was read with a copper-constantan thermocouple. Since the noise and stability of the detector signal were sensitive functions of the temperature of the detector coil, it was necessary to use the dewar vessel to prevent any variation in the temperature of the pick-up coil.

However, introduction of the dewar vessel walls and vacuum space inside the pick-up coil markedly reduced the filling-factor, resulting in weak signals and poor signal-to-noise ratios. Consequently only shift values were obtainable at the higher temperatures.

RESULTS AND DISCUSSION

The data on the frequency shifts and line widths are presented in Table I. Knight shift changes from pure cadmium are expressed in percent of the pure cadmium shift at each temperature, rather than being expressed as percent change from the cadmium shift at a single temperature. All line widths are experimental peak-to-peak widths of the observed absorption derivative. At room temperature, where, due to the large anisotropic Knight shift, the lines are markedly asymmetric, the line widths recorded are taken between the two outermost peaks in the derivative curves.

Fig. 11 shows the change in Knight shift versus concentration of indium at 78°K and 300°K for the cadmium-indium series of alloys.

Fig. 12 shows ΔK versus temperature for $Cd^{3/4}$ In and Cd^{1} In. (The notation here, which is not standard, has the following meaning: the first symbol listed is the solvent metal -- cadmium, in all of the alloys studied. The superscript denotes the concentration, in atomic percent, of the solute metal, which is immediately followed by the chemical symbol of the solute metal. Thus, Cd^{1} In denotes a binary alloy of cadmium and indium consisting of 99 atomic percent cadmium and 1 atomic percent indium.) Although all observed shift values are quite small, it is interesting that the largest shifts appear at the lowest temperature and for the smallest concentration. ΔK is clearly seen not to be simply proportional to concentration for these alloys. The small changes in electron concentration

TABLE I

Knight Shifts and Line Widths

	4.2°K $\Delta K/K_{cd}$(%)	Linewidth (kHz)	78°K $\Delta K/K_{cd}$(%)	Linewidth (kHz)	300°K $\Delta K/K_{cd}$(5)	Linewidth (kHz)	423°K $\Delta K/K_{cd}$(%)
Cd	0	3.4	0	1.7	0	5.87	0
$Cd^{1/4}$ In			-1.24	2	-1.95	5.80	
$Cd^{1/2}$ In			-0.75	1.8	-0.43	5.66	
$Cd^{3/4}$ In	-5.7	2.6	-0.99	1.6	-1.52	6.10	
Cd^{1} In	-2.9	2.6	+0.25	1.4	-0.76	4.65	0
$Cd^{1.2}$ In			-0.50	1.5	-0.33	5.95	
$Cd^{1/2}$ Ag	+3.3	4.0	+3.72	2	-2.60	5.44	
Cd^{2} Ag	+7.15	4.5					
Cd^{3} Mg	-2.2	2.7	-1.1	2.5	-5.85	5.87	0
Cd^{4} Mg	+3.5	3.8	+1.24	2.7	-5.64	5.58	
Cd^{5} Mg	0	3.8	+2.50	3	-9.00	5.95	

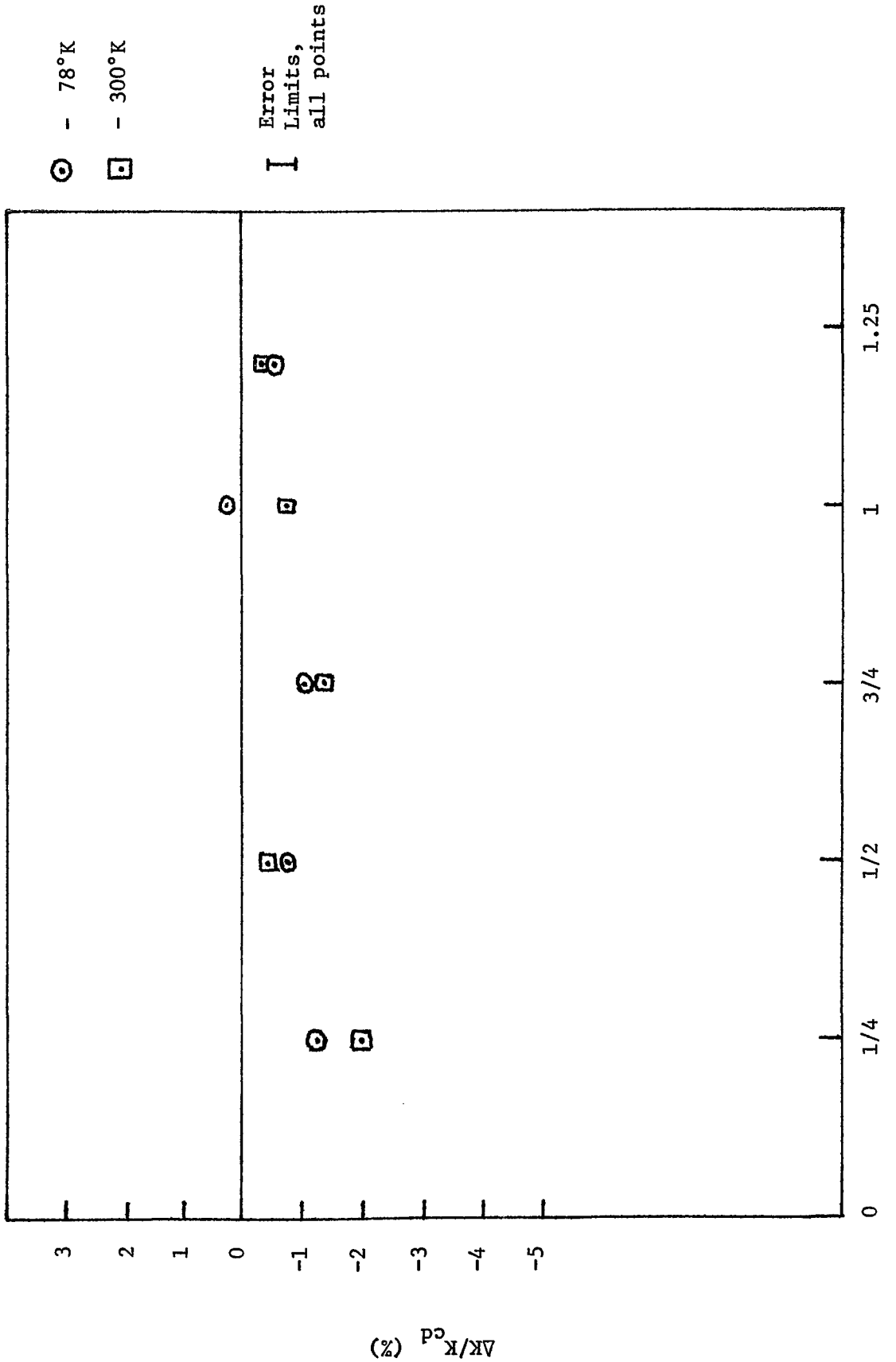

Figure 11. $\Delta K/K_{cd}$ Versus Indium Concentration

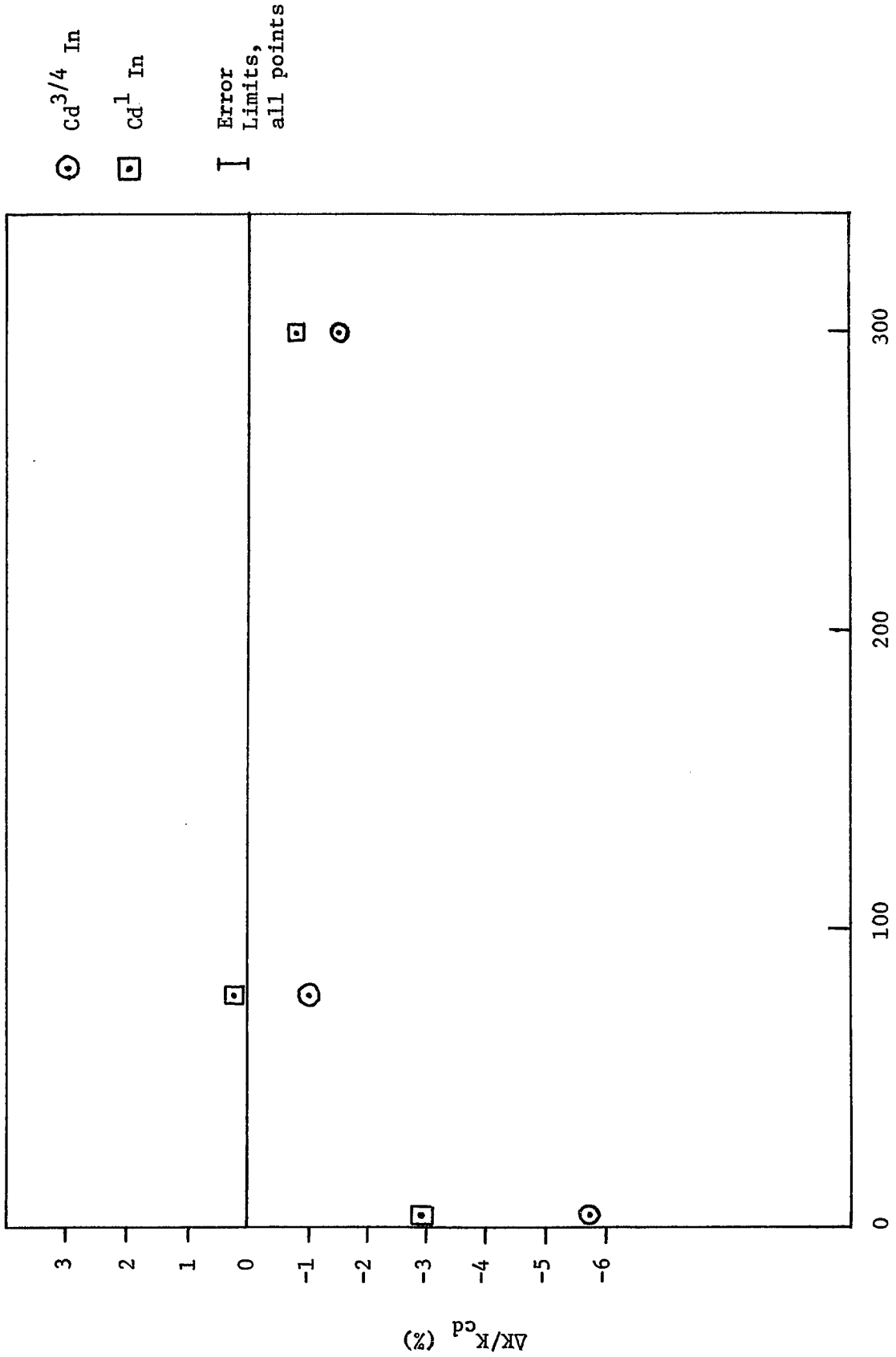

Figure 12. $\Delta K/K_{cd}$ Versus Temperature, Cadmium-Indium Alloys

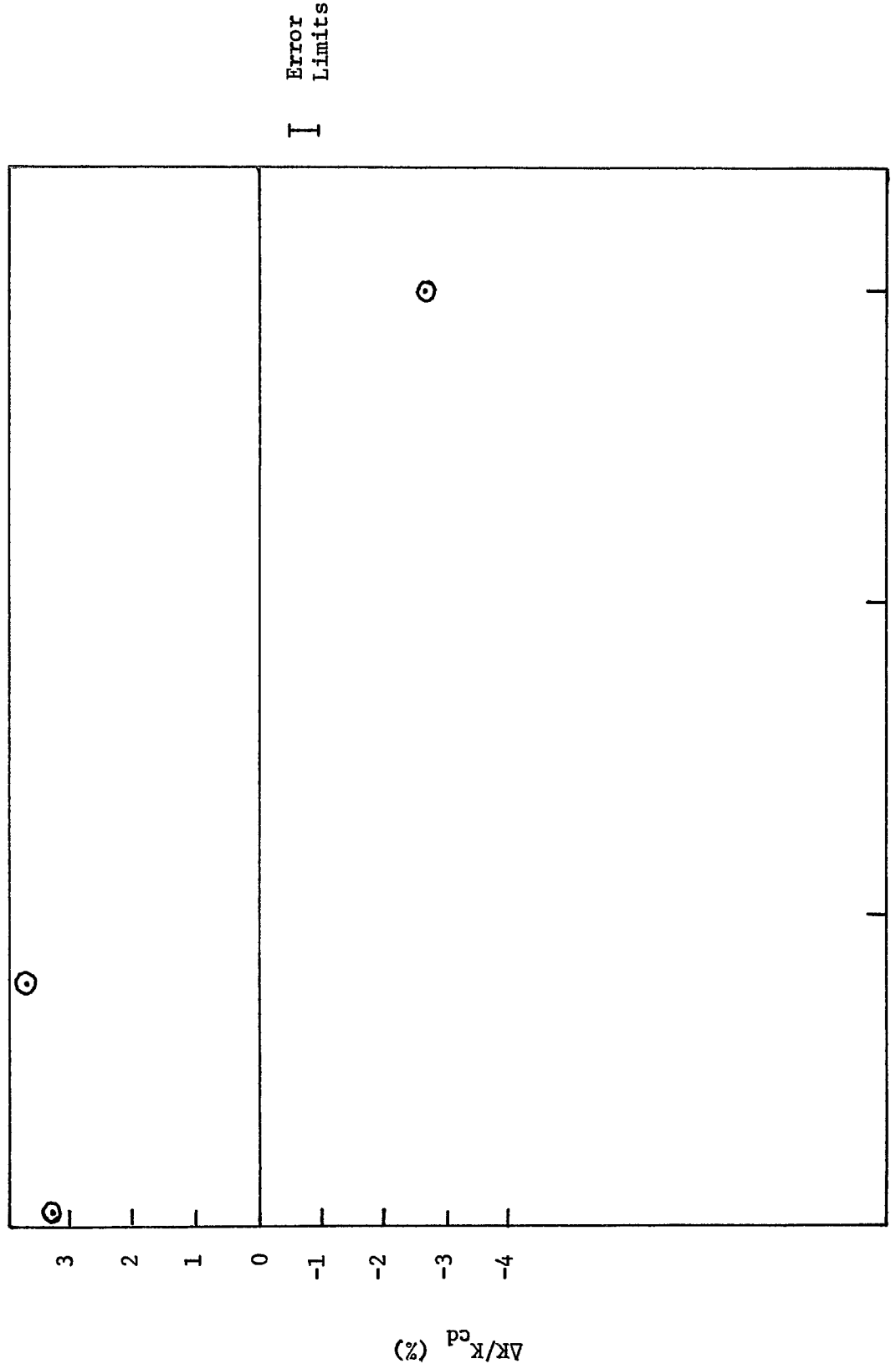

Figure 13. $\Delta K/K_{cd}$ Versus Temperature, $Cd^{1/2}$ Ag

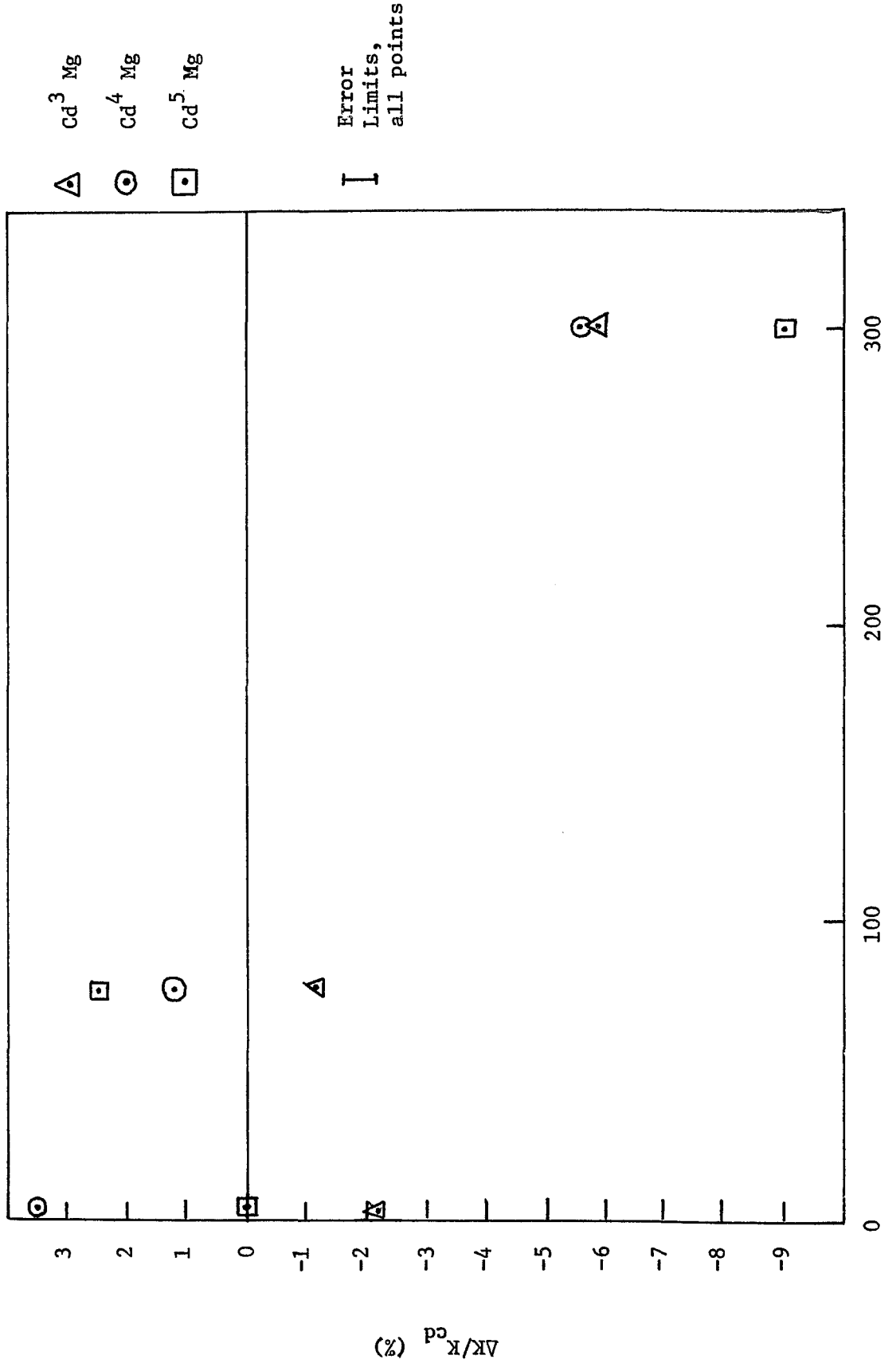

Figure 14. $\Delta K/K_{cd}$ Versus Temperature, Cadmium-Magnesium Alloys

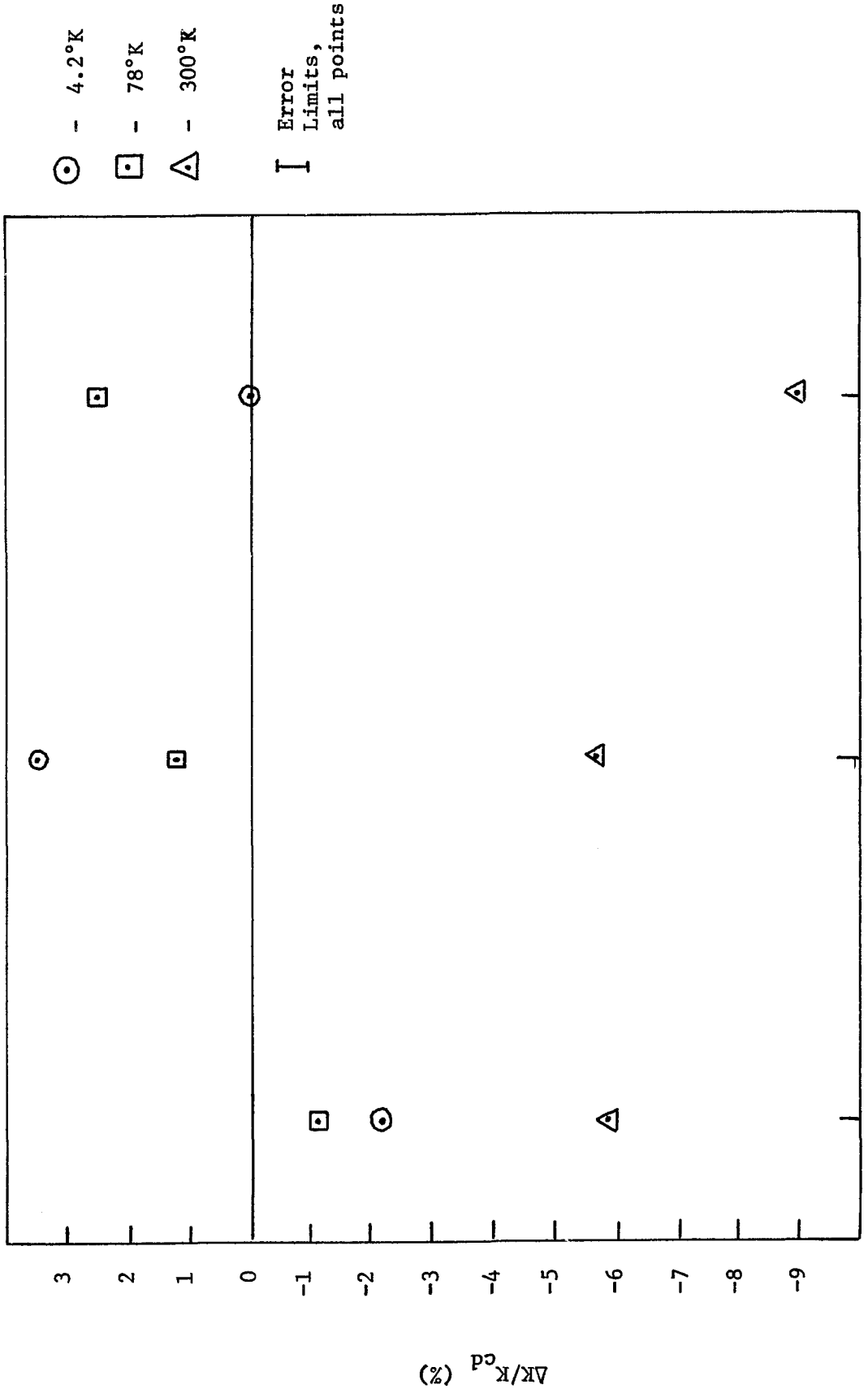

Figure 15. $\Delta K/K_{cd}$ Versus Mg Concentration

achieved in the cadmium-indium series of alloys do not appear to significantly alter the temperature variation of the cadmium Knight shift. Since no data is available on c/a ratios or thermal or elastic properties for cadmium-indium alloys, it is hazardous to speculate on causes of the observed shifts.

Fig. 13 shows ΔK versus temperature for $Cd^{1/2}$ Ag. The magnitude of the shifts is much greater than those in the cadmium-indium series of alloys. At 4.2°K, where it was possible to observe an NMR line for Cd^{2} Ag, the shift, ΔK, increases with concentration of silver. Inhomogeneous Knight shift broadening is apparent in the line widths at 4.2°K, and may be inferred to be present at 78°K and 300°K by the inability to obtain an NMR line for Cd^{2} Ag at those temperatures.

Fig. 14 shows the variation in ΔK with temperature for the cadmium-magnesium alloys. Fig. 15 displays ΔK as a function of concentration for the cadmium-magnesium alloys at 4.2°K, 78°K, and 300°K. For these alloys the shifts are largest at room temperature, contrary to the behavior observed with the cadmium-indium series. At 4.2°K and 78°K the shifts change sign with concentration of magnesium. ΔK does not appear to be simply proportional to the magnesium concentration. At 78°K the line widths increase with magnesium concentration, but not at 4.2°K or 300°K.

The dramatic changes in magnetic susceptibility produced by adding magnesium to cadmium which were observed by Verkin, et.al.,[9] do not appear in the Knight shift data. Since the interband term invoked by him to explain his susceptibility data enters into the diamagnetic susceptibility of the electrons, which contributes to the Knight shift through an

orbital contribution, it is concluded from the present data that even though small pockets of electrons of low Fermi temperature, associated with small energy gaps and interband transitions are important to the magnetic susceptibility, they are relatively unimportant in the Knight shift behavior. Thus the small energy gap and interband transitions associated with the portion of Fermi surface about points K in the Brillouin zone may be eliminated as sources for the temperature dependence of the cadmium Knight shift.

Changes in the c/a ratio produced by addition of magnesium are considerable -- the decrease in the c/a ratio from pure cadmium in going to Cd^5 Mg is 1.3%, comparable to the change in c/a in pure cadmium obtained by varying the temperature from 4.2°K to the melting point.[43] Addition of silver to cadmium also decreases the c/a ratio, even more rapidly than the addition of magnesium.[37] If the c/a ratio variation with temperature were the primary source of the variation of the cadmium Knight shift larger effects on ΔK should have appeared in these measurements, unless a competing effect associated with the alloying was opposing the influence of changes in the c/a ratio. No evidence for such a competing effect is available. The isothermal Knight shift measurements on cadmium as a function of pressure made by Kushida and Rimai[14] also suggest that changes in the c/a ratio are not the primary source of the thermal variation of the Knight shift in cadmium.

A prominent feature of the data not appearing in the table of shifts and linewidths is the difference in line shape between the Cd-Mg alloys and the other alloys and pure cadmium. Figure 16 shows an experimental NMR line for Cd^1 In; an experimental NMR line for Cd^4 Mg is shown

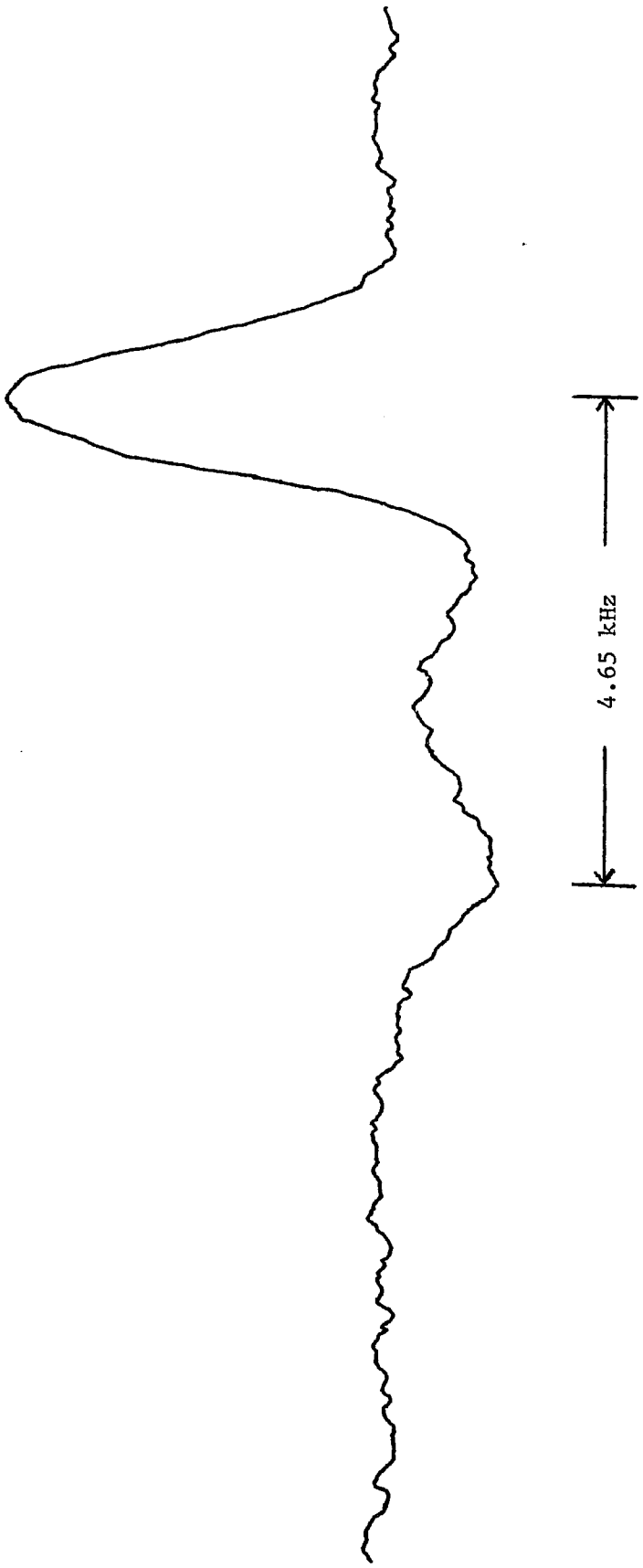

Figure 16. Experimental NMR Line For Cd^{1} In At 300°K And 12 Kilogauss

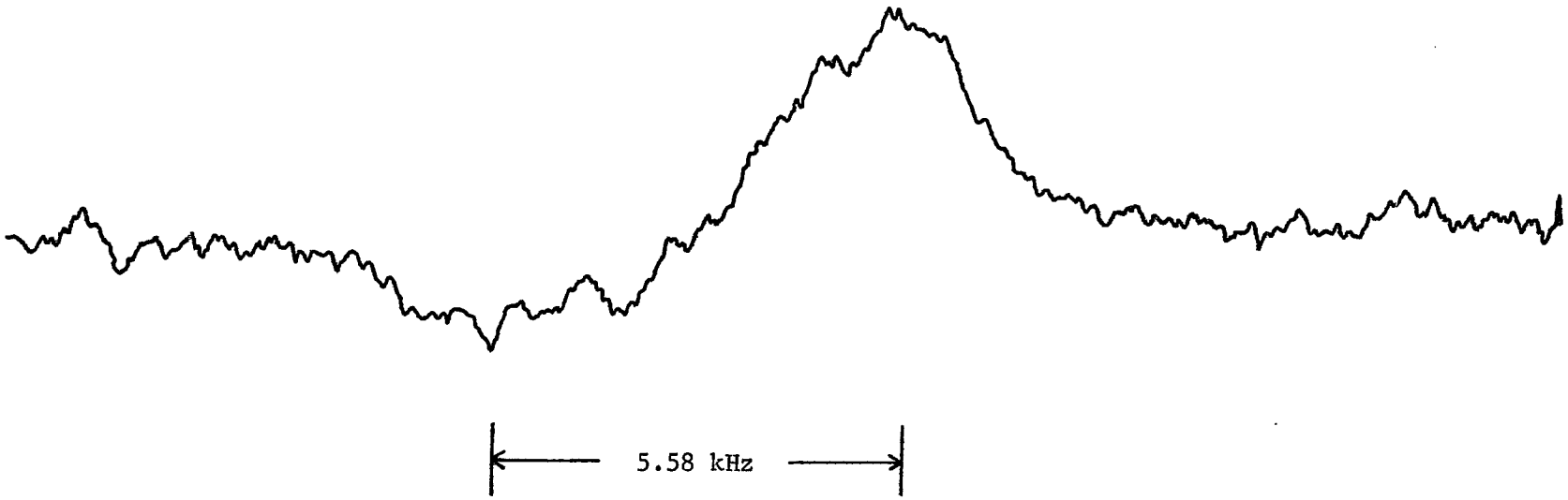

Figure 17. Experimental NMR Line For Cd^{4} Mg At 300°K And 12 Kilogauss

in Figure 17. The extra peak occurring in Cd and Cd-In and Cd-Ag alloys at room temperature, due to large K_{an}, does not appear for the Cd-Mg alloys. A possible explanation might be that the addition of magnesium impurities to cadmium tends to decrease the anisotropic Knight shift. On the other hand the over-all line width does not appear to be significantly affected. Since this point may be more comprehensible after a discussion of the factors contributing to the line widths and shapes, its consideration will be resumed later.

Possible contributions to the line widths in the cadmium alloys are the following: (1) the dipolar line width; (2) the anisotropic Knight shift broadening; (3) inhomogeneous Knight shift broadening; (4) lifetime broadening; (5) indirect exchange broadening; (6) pseudodipolar broadening.

The dipolar line width is the portion of the line width due to the magnetic dipolar interaction between the nuclear magnetic moments; this contribution is calculable by the celebrated Van Vleck second-moment relation.[44]

The anisotropic Knight shift broadening has already been discussed in the theory section. It appears when using polycrystalline samples. Bloembergen[45] has obtained an expression for the functional form of this contribution in the case of metals with axial symmetry.

The inhomogeneous Knight shift broadening refers to the field dependent broadening produced by the Friedel oscillations in the electronic charge distribution about impurities in the alloys.

Lifetime broadening, sometimes called spin-lattice relaxation broadening, is a consequence of the Heisenberg uncertainty relation and

is significant only in the event of very short spin-lattice relaxation time.

Indirect exchange broadening and pseudodipolar broadening arise from indirect interactions between the nuclear magnetic moments, the former mediated via the conduction electrons through the hyperfine contact interaction, the latter via the conduction electrons through the dipolar term in the hyperfine interaction. Indirect exchange has been treated by Ruderman and Kittel;[46] pseudodipolar interactions were discussed by Bloembergen and Rowland.[47]

Masuda[48] has discussed the contributions to the line width in pure cadmium. Based on a direct measurement of the spin-lattice relaxation time, T_1, which he found to be 0.5×10^{-3} sec at room temperature, he concluded that the T_1 contribution to the width was small ($\sim$ 0.2 gauss). The dipolar width was also small. Masuda[48] estimated that indirect exchange broadening and pseudodipolar broadening were the major contributors to the line width in pure cadmium, exclusive of the field-dependent effects of the anisotropic Knight shift in powder samples. He estimated the ratio of pseudodipolar contribution to the indirect exchange contribution as 0.3.

In discussing line shapes, it is convenient to lump items (1), (4), (5), and (6) together and call the result the static symmetric broadening, whose shape function, f, may be more or less approximated by a Gaussian curve. Calling the shape function for the field dependent anisotropic Knight shift broadening g, the over-all line shape, F(y), may then be expressed as the convolution $F(y) = \int_{-\infty}^{\infty} g(x)\, f(x - y)\, dx$, where y

is a normalized field or frequency variable. An appropriate choice of f and g then permits a relatively good fit to the experimental line shapes for pure cadmium. The shape of the resulting line is sensitive to the relative magnitudes of the anisotropic Knight shift and the static symmetric broadening.

Borsa and Barnes[18] apply the above routine to a systematic study of cadmium NMR lines. By extrapolating their line width measurements to zero field they obtain a value for the static symmetric broadening of 0.5 gauss, compared to Masuda's value[48] of 1.5 gauss. In disagreement with Masuda, they conclude that this small value of 0.5 gauss is consistent with a mainly nuclear dipolar source of symmetric broadening. Masuda's value for the cadmium NMR line width was in error, probably as a result of inhomogeneous field broadening. However, from the accepted value of 0.23 gauss for the pure dipolar broadening contribution, it is concluded that the indirect exchange broadening and pseudodipolar broadening do contribute to the cadmium NMR line width, but to a much smaller degree than alleged by Masuda.

The purpose of discussing the line shape analysis routine was to clarify the dependence of line shape upon the anisotropic Knight shift. Whenever the static symmetric broadening is small compared to the anisotropy, both line shape and line width will be dominated by the anisotropic Knight shift broadening. At low temperatures, when the value of K_{an} is small, the shape and width of the NMR lines reflect this smallness. At high fields, and for non-negligible anisotropy, the line width is determined by the anisotropy. Unfortunately, however, when considering the NMR line shapes

in the cadmium alloys, the inhomogeneous Knight shift must be brought into the picture.

In treating the inhomogeneous Knight shift broadening due to Friedel oscillations Blandin and Daniel[19] assume that this broadening may be lumped with the static symmetric broadening. It should be pointed out, however, that the inhomogeneous Knight shift broadening is not strictly a symmetric broadening mechanism. Blandin and Daniel did not treat the case in which the solvent NMR line displays an anisotropic Knight shift, and Borsa and Barnes did not include the inhomogeneous Knight shift in their line shape analysis, since they were not studying alloys. Line shape calculations from first principles are exceedingly difficult and have not yet been performed even in simple cases. The general area of NMR line shapes, including the effects of both the anisotropic and the inhomogeneous Knight shifts would seem to be a worthy topic for theoretical investigation.

Impurity scattering and the attendant phase shifts can modify the anisotropic Knight shift in alloys. Snodgrass and Bennett[49] have discussed this point in connection with their study of the NMR of ^{207}Pb in Pb-In alloys. Since lead is cubic, its NMR ordinarily has no anisotropic Knight shift; however, as a result of the deviation from local cubic symmetry at the ^{207}Pb sites produced by the addition of In atoms, an anisotropy is induced. Snodgrass and Bennett argue that this anisotropy provides an observable contribution to the NMR line width in the Pb-In alloys, although admitting that the effect and observability of this anisotropy are still active issues. Concentrations of indium as high as 20% were employed in these studies.

In the present investigation on cadmium alloys there is an intrinsic anisotropy even before alloying. It is felt that for the low concentrations of impurities in the alloys studied in this research Friedel oscillations effects on the anisotropy are small. The absence of any obvious shape changes in the NMR lines of either the Cd-In alloys or the $Cd^{1/2}$ Ag alloy lend some support to this contention. It is concluded from the difference between the shape of the Cd-Mg NMR lines and the shape of the NMR lines of the other alloys that a decrease in K_{an} on alloying magnesium is consistent with the data and with current theories on NMR line shapes in alloys.

Since the c/a ratio decreases with increasing concentration of magnesium, as it does for decreasing temperature, and K_{an} is known to decrease with decreasing temperature, it may be reasonable to expect a decrease in K_{an} (at a fixed temperature) with alloying magnesium.

Since the anisotropy in the Knight shift of cadmium, according to Kasowski and Falicov,[7] depends on a delicate, temperature sensitive balance between the p_z-character of states on the third zone lens with the p_x-p_y-character of states on the second zone monster, it is conceivable that c/a changes, as produced by alloying, could modify this balance and provide the posited variation in anisotropy suggested to account for some of the line width and line shape data. One might speculate that since the second zone monster varies more with temperature than the third zone lens, it is changes in the second zone monster that lead to the putative decrease in anisotropy in the Cd-Mg alloys. However, in this connection please refer to the discussion below in which it is indicated that lattice vibration effects are more important than changes in the c/a ratio.

At 78°K, where the anisotropy has become small, the increase in line width with concentration in the Cd-Mg alloys may be attributed to inhomogeneous Knight shift broadening. This may also be inferred for the Cd-Ag lines at both 4.2°K and 78°K. It is felt that the absence of any increase in line width with concentration of indium implies a decrease in anisotropy with alloying, which counteracts the Friedel oscillation broadening mechanism. It is possible that Friedel oscillations effects on the anisotropy itself may be contributing here. The distinctly smaller line width obtained in the Cd^{1} In sample at 300°K and at 78°K indicates a decreased anisotropy.

In the Kasowski-Falicov theory the temperature dependence of K_{iso} in cadmium is a consequence of the largeness, the pronounced d-character, and the consequent anisotropy of the pseudopotential, in conjunction with the tendency of the lattice vibrations to weaken the pseudopotential and render it more isotropic and free-electron like. Changes in lattice parameters, and thus also the c/a ratio, appear to be less effective in determining the thermal behavior of K_{iso} than the lattice vibrations; this opinion is suggested by both the present data, wherein large c/a changes induced by alloying provide only small changes in K_{iso}, and that of Kushida and Rimai[14] revealing only small effects on K_{iso} of very high hydrostatic pressures.

If one assumes that adding small concentrations of impurities would have only a small influence on the strength and character of the pseudopotential, one could then argue that the major effect of alloying on the temperature dependence of K_{iso} would result from changes in the phonon spectrum and phonon wave functions. Any differences in the phonon

spectrum would appear in the pseudopotential calculations through the Debye-Waller factors that introduce lattice vibration effects into the calculations. Both the ionic masses and the phonon frequencies appear in the Debye-Waller factors. Since silver and indium differ in atomic number from cadmium by only one unit, they have nearly the same masses as cadmium and might therefore be expected to alter the lattice vibration effects to a negligible extent. The introduction of magnesium, however, having an atomic weight of only 24.312 compared to the value 112.40 for cadmium, might be expected to have a more pronounced influence on the lattice vibrations and thus on the thermal variation of K_{iso}. It is interesting in this regard that the largest observed deviation from K_{iso} of cadmium occurred with the Cd-Mg alloys -- for the highest magnesium concentration and at room temperature, the highest temperature at which reliable data were obtained.

Data obtained on Cd^{1} In and Cd^{3} Mg at a temperature of 423°K have not been plotted because it was felt that the experimental uncertainties inherent in the measurements render them unreliable. No change in K_{iso} at that temperature was observed within the experimental error, estimated to be about 10% of the 4.8 kHz shift of the pure cadmium resonance away from its room temperature value.

The lack of a simple proportionality between ΔK and concentration in the cadmium-indium alloys indicates that in some cases band effects are more important than Friedel oscillations in determining the effects of alloying on the NMR lines. These results on the cadmium-indium alloys are consistent with the conjecture of Watson, Bennett, and Freeman[28] that

the dependence of ΔK on concentration may not be a linear one, and with their opinion that the low concentration region might provide more rapid variations of ΔK with concentration than the higher concentration regions generally investigated and invoked in support of the scattering theory prediction of a linear variation.

In conclusion, no significant changes in the behavior of K_{iso} in cadmium with temperature have appeared as the result of alloying small amounts of indium, silver, and magnesium with cadmium. The generally small values of the changes in K_{iso} appear to be consistent with predictions of either the Friedel oscillation theory of Blandin and Daniel[19] or the rigid band picture proposed by Watson, Bennett, and Freeman.[28] Comparison of the Knight shift data in the cadmium-magnesium alloys with the susceptibility data of Verkin, et. al.,[9] on cadmium-magnesium alloys indicates that the c/a ratio variation in cadmium with temperature is not the primary source of the temperature dependence of the isotropic Knight shift in cadmium. The NMR data obtained in this research on the cadmium-magnesium alloys also appear to rule out any connection between the temperature dependence of K_{iso} in cadmium and variation of small pieces of the Fermi surface centered about point K in the Brillouin zone. In order to interpret the pronounced difference in shape of the cadmium-magnesium NMR lines from that of pure cadmium NMR lines and of the other alloy NMR lines, it is suggested that the anisotropic Knight shift is decreased by the addition of magnesium, and an interpretation of this decrease is offered in terms of the theory of Kasowski and Falicov.[7]

It is suggested that the smallness of the observed changes in K_{iso} and the absence of any appreciable modification of the thermal

behavior of K_{iso} of cadmium upon alloying are consistent with the pseudopotential theory of Kasowski and Falicov, and that modifications of the phonon spectrum have more influence on the thermal behavior of K_{iso} than small, alloy-induced variations in the pseudopotential or changes in the c/a ratio produced by alloying.

The data obtained in this study on the Knight shift in the cadmium-magnesium alloys appear to be in good agreement with some recent measurements by E. Dickson.[50] He has determined the Knight shift in $Cd^{9.4}$ Mg at several temperatures from 78°K up to the melting point and has observed no significant difference in the temperature variation of K_{iso} from that of pure cadmium.

The results of this study are also consistent with the observation of Rigney and Flynn,[51] based on their own data on alloy series using In, Sb, and Al as solvents, and the data of Snodgrass and Bennett[52] on lead alloys, that the polyvalent metals show an unusual stability of the Knight shift against alloying.

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